Development of Polylactic Acid-Polyhydroxybutyrate Blends for Packaging Applications

A thesis submitted in fulfilment of the requirements for the degree of Master of Engineering

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DECLARATION

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

DEHAO KONG

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ABSTRACT

Until recent years, the packaging materials which are based on non-renewable fossil resources have been used widely. However, the toxic or noxious components released during manufacture and their non-degradability cannot be ignored. Therefore, the environmental friendly and renewable materials are currently receiving more attentions by researchers and commercial packaging materials producers. In flexible packaging industry, a biodegradable material, polylactic acid (PLA) has significant potential as it offers high clarity and stiffness, together with excellent printability. On the other hand, poly (hydroxybutyrate) (PHB), the best-known poly(hydroxyalcanoate) (PHA) synthesized by controlled bacterial fermentation, presents high crystallinity which is required for film blowing application. However, the main drawback of PHB is that its melting temperature is about 170–180 °C, which is close to the degradation temperature. This presents a relatively small processing window for melt extrusion. Nevertheless, the melting temperature of PHB can be lowered far below its thermal decomposition temperature to make this material much easier to process either through chemical modifications or blending with another polymer. Since PLA and PHB present similar melting temperatures, they can be blended in the melt state to produce a new biodegradable material that combines the advantages of both polymers.

This thesis reports on research conducted to improve PLA's properties to satisfy final applications such as packaging. PLA was blended with PHB in various concentrations (0, 10, 20, 25, 30, 40, 50, 60, 70, 80, 90 and 100 wt%). The main focus of this work is to analyse the rheological and thermal properties of these PLA/PHB blends.

The thermal results indicated that the PLA/PHB blends are immiscible but existed molecular interaction between two polymers over the entire blends range. The remarkable separate peaks of the melting temperature in the blends correspond to the melting temperature of pure PLA and PHB. The crystallization of PLA was enhanced in the PLA/PHB blends as the PHB content was increased up to 25 wt%. This could be due to PHB acting as a nucleating agent in PLA and high crystalline structure of PHB.

Dynamic rheological tests were carried out for all PLA/PHB blends mentioned earlier to study the effect of the PHB concentration into PLA at three different temperatures (180, 190 and 200 ℃). As expected, increasing temperature was led to a decrease of the storage and loss moduli as well as dynamic viscosity values of all PLA/PHB blends. The time-temperature superposition (TTS) principle, based on the Arrhenius approach, was used to collapse all three rheological curves at 3 different temperatures into a master curve successfully. TTS was enabled the rheological properties of PLA/PHB blends to be extended on either side of the original frequency range tested depending on the selected reference temperature.

It was observed that PLA/PHB Blends containing low PHB content (0-40 wt%) produced higher dynamic viscosity and elastic properties compared to pure PLA. However, for PLA/PHB Blends containing higher PHB content (> 60 wt%), their rheological properties were between that of the two pure materials. At low PHB content, the PLA/PHB blends showed positive-deviation, according to the mixing rule. They also showed typical liquid-like, temperature-dependency and shear-thinning behaviour as well.

The optimum PLA/PHB blends, based on the rheological and thermal properties, were found to be those containing 20-25 wt% PHB content. These blends (PLA75/PHB25 and PLA80/PHB20) can be considered for use in packaging applications.

Nomenclature

PLA	Poly (lactic acid)
PHB	Poly (hydroxybutyrate)
PHA	Poly (hydroxyalkanoate)
M_w	Molecular weight
T_m	Melting temperature (°C)
T_g	Glass transition temperature (°C)
ρ	Density (g/cm^3)
σ	Tensile strength (Mpa)
E	Elasticity (Gpa)
MDSC	Modulated differential scanning calorimetry
ARES	Advanced research grade rheometer
G'	Storage modulus (Pa)
G"	Loss modulus (Pa)
η'	Dynamic viscosity (Pa-s)
a_T	Shift factor
η(ω)	Viscosity function
E_0	Fluid activation energy (J/mol)
R	Universal gas constant (J/molK)
T_{cc}	Cold crystallization temperature (°C)
X_c	Crystallization (%)

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Chapter 1 Introduction

1.1 Overview

In recent years, sustainability, environmental concerns and green chemistry have played a big role in guiding the development of the next generation of materials, products and processes. The persistence of plastics in the environment, dwindling petroleum resources, shortage of landfill space and the concerns over emissions of toxic gases during incineration have motivated researchers and scientist to develop biodegradable polymers from renewable resources. Particularly, renewable agricultural and biomass feedstock have shown much promise for use in eco-efficient packaging to replace petroleum feedstock without competing with food crops.

Poly (lactic acid) (PLA) is a biodegradable and biocompatible crystalline polymer that can be produced from renewable resources. PLA is of great interest to the packaging industry due to its many advantages such as high transparency, availability in the market, ease of processing, economically competitive and environmentally benign characteristics (Armentano et al., 2013). In view of the fact that PLA also shows some poor barrier properties, hence increasing PLA crystallinity becomes necessary for the intended use. Thus, melt blending PLA with another more crystalline biopolymer with similar melting temperature, such as poly(hydroxyalkanoates) (PHAs), has gained considerable attention for the food packaging sector. Among PHAs, poly(hydroxybutyrate) (PHB), produced by controlled bacterial fermentation, is one of the most common representatives of PHA. PHB has also been widely studied for food packaging applications as well (Zhang & Thomas, 2011).

PHB is a polymer in the polyhydroxyalkanoate (referred to as PHA) family, which is synthesized by bacteria as an energy storage mechanism. PHB is completely biodegradable and has suitable mechanical properties for use as a bulk polymer. It has also found use in a number of biomedical applications in part due to its biodegradability (Zhang et al., 1995 and Zhang et al., 2010). Ideally, PHB or a similar biodegradable material would replace non-biodegradable polymers as the material of choice for packaging and cheap moulded articles, thus greatly reducing the amount of non-biodegradable waste production. Whilst PHB has been widely studied (Nitin 2006 and Furukawa et al., 2005), it has not been widely used as a commodity material yet due to its high price, brittleness, poor processability and low melt-strength due to serious thermal degradation.

PHB had been produced industrially as its copolymer with hydroxyvalerate since the late 1960s, under the trade name Biopol®, by Zeneca, an ICI subsidiary (Zhang et al., 1995). However, the

demand for biodegradable polymers has only recently been great enough to support investment in this field: in the last decade, multi-ton PHA production has been announced by companies in the United States, Brazil, Europe and China (Hu et al., 2008). While production volumes are still relatively low, the market for PHAs is expected to increase over the next decades.

Adoption of PHB as a commodity copolymer is currently constrained by two significant shortcomings. First, although the polymer is stiff, it becomes increasingly brittle as it ages. Packaging materials made from such a brittle material would be prone to cracking under even very small deformations. Second, the polymer is subject to a severe degradation mechanism that complicates processing. A significant amount of research has been invested in developing an improved PHB-based material, with some success. For instance, PHB-PHA copolymers are more ductile and can be processed at lower temperature while retaining biodegradability. A range of PHB blends with improved mechanical properties has also been reported (Furukawa et al., 2005, Hu et al., 2008, Abdelwahab et al., 2012), although PHB tends to blend best with chlorine-containing polymers which are not biodegradable and are often toxic.

The present work focuses on PLA/PHB blends prepared by melt compounding. In this work, 12 different blends of PLA/PHB (100/0, 90/10, 80/20, 75/25, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100) have been prepared and characterized. The rheological properties were analysed by the Advanced Rheometrics Expansion System (ARES) rheometer at three different temperatures 180 °C, 190 °C, and 200 °C. The thermal properties of these blends were characterized by modulated differential scanning calorimetry (MDSC) to explore their thermal behaviours.

Currently, there is very limited work reported in the literature on rheological properties of PLA/PHB blends, despite the fact that PLA/PHB blends have been used to produce packaging films on a lab scale basis. This project focuses on the characterisation of PLA/PHB blends' thermal and rheological properties to determine their suitability for producing packaging films

1.2 Research Aims, Objectives and Questions

Research Aims

The aim of this research project is to examine the effect of temperature and concentration on the rheological and thermal properties of PLA/PHB blends as well as recommending the optimum composition of the PLA/PHB blends for use in packaging applications.

Objectives

1. To investigate the effect of concentration on the rheological properties of PLA/PHB blends.
2. To investigate the effect of temperature on the rheological properties of PLA/PHB blends.
3. To investigate the thermal properties of PLA/PHB blends.

Research Questions

1. What it the effect of concentration on the rheological properties of PLA/PHB blends?
2. What is the effect of temperature on the rheological properties of PLA/PHB blends?
3. What is the optimum composition of PLA/PHB blend for use in packaging applications?

1.3 Structure of the Thesis

The thesis consists of the following chapters:

- Chapter 1 gives an introduction and background information justifying reasons for carrying out this work.
- Chapter 2 contains a comprehensive literature review on rheological and thermal results of PLA/PHB blends.
- The experimental methodologies, equipment and procedures as well as analysis of errors associated with the experiments are presented in Chapter 3.
- Chapter 4 presents the properties of PLA/PHB blends, which include the effect of concentration and temperature on the rheological properties of PLA/PHB blends and the MDSC results of PLA/PHB blends.
- Chapter 5 presents the main conclusions and provides some recommendations for future work.

Chapter 2 Literature Review

This section presents a background of biodegradable polymers and a comprehensive literature review on thermal and rheological results of PLA-based or PHB-based blends.

2.1 Background of Biodegradable Polymers

The first synthetic polymer was invented by Leo Hendrik Baekeland in 1907. This was a thermosetting phenol-formaldehyde resin called Bakelite. In recent decades, the rapid development of polymers has made a large contribution to technology with the invention of a highly effective catalytic polymerization process. Because commodity polymers-polyethylene, polypropylene, polystyrene and poly (vinyl chloride) (PVC) can be produced so cheaply, their use has been exploited for the mass production of disposable packaging materials. Thus, around the world, polymer pollution has become a serious issue as these polymers are not biodegradable. This, together with the reducing reserves of crude oil, encourages research into the development of renewable and biodegradable sources of raw materials for producing polymers. Figure 2.1 shows the general trend of polymer development globally.

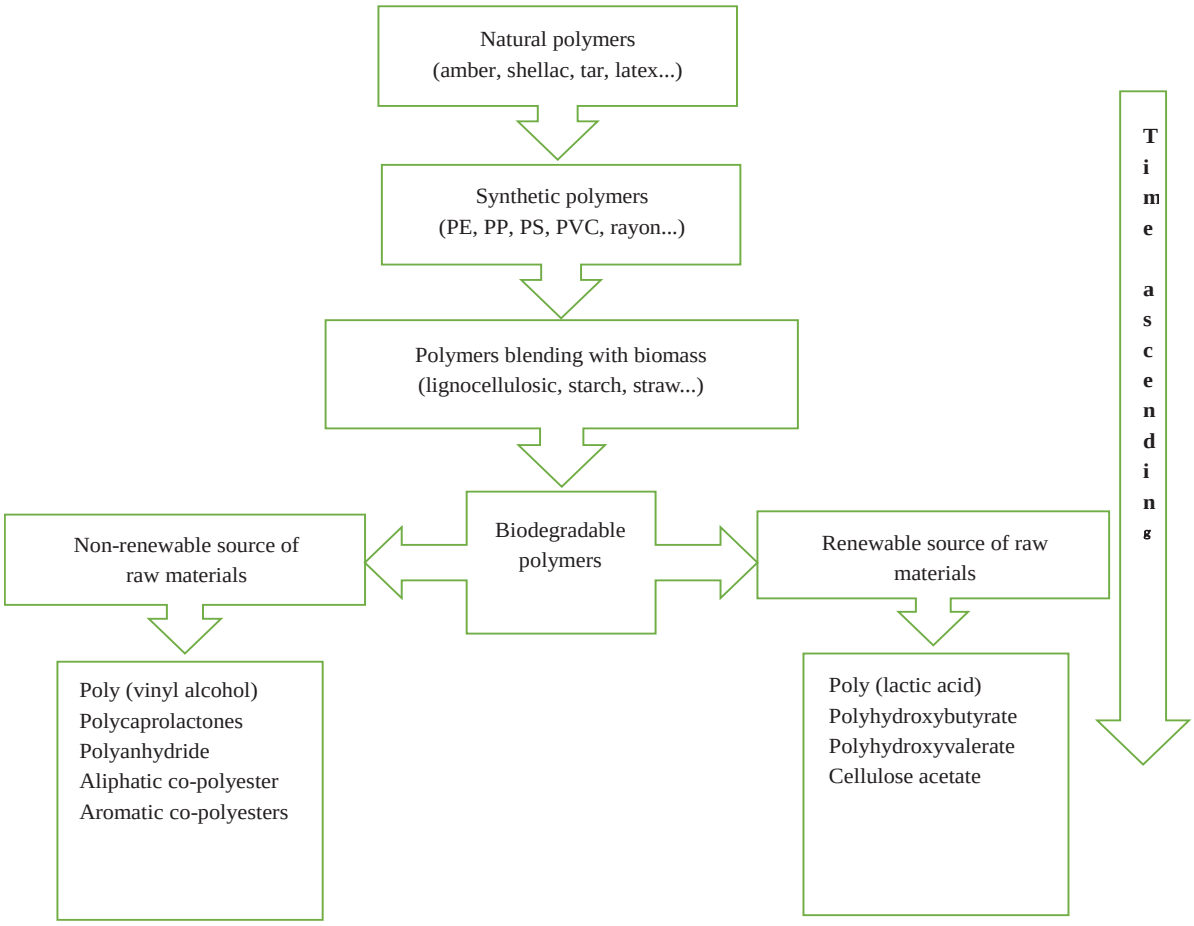


Figure 2. 1 Trends in polymer development

Although steps have been taken to educate people about the environmental impact caused by the exploitation of plastics, these materials continue to represent the largest proportion of domestic waste. Conventional plastic waste takes a very long time to be broken down into harmless substances compared with organic material. For instance, a telephone top-up card takes over 100 years to naturally degrade, while an apple core requires just 3 months to be naturally transformed into organic fertilizer (Economic Assessment Office, 2007). Due to the better degradability of biomass over conventional plastics, polymer-biomass blends are the first step in providing alternatives to help reduce plastic waste problems. Generally, abundant biomass such as lignocellulosics and starches are blended with synthetic polymers. These polymer compounds are partially degradable by microorganisms. However, after the biomass portion has been consumed, the leftover polymer skeleton will still cause harmful effects to the environment.

The focus is then on developing environmentally friendly polymers. These polymers are naturally degradable when disposed in the environment. The carbon footprint of production of these polymers is monitored to ensure sustainable environmental protection. There are some biodegradable polymers on the market; these are listed in Table 2.1. These polymers are only produced on a small scale, primarily for biological applications, but also for exploration of commercial potential. Most of the biodegradable polymers are in the polyesters group. Biodegradable polymers can be derived from renewable and non-renewable sources. Useful biodegradable polymers are not limited to neat polymers, but also include copolymers (polymerization of different monomers), the latter having improved biodegradability and structural properties.

Table 2. 1 Some Common Biodegradable Polymers

Polymer	**Applications**	**Biodegradability**
Polycaprolactone (PCL)	Suture	>12 months
	Paint and mental protection film	
Polyhydroxybutyrate (PHB)	Consumer packaging	3-12 months
Polyhydroxylvalerate (PHBV)	Compost bags	
Polylacticacid (PLA)	Food packaging bags	3-12 months

2.2 Poly lactic acid

Poly (lactic acid) (PLA) is one of the first commodity polymers produced from annually renewable resources with excellent properties comparable to many petroleum-based plastics (Martin and Averous, 2001). Some of the environmental benefits of PLA and opportunities for the future are presented by Henton et al. (2005). These include PLA requiring less energy to produce as well as reduced green-house gas production. PLA resin has high mechanical properties, thermal plasticity, processing properties, and biocompatibility and has been

proposed as a renewable and degradable plastic for uses in service ware, grocery, waste-composting bags mulch films, controlled release matrices for fertilizers, pesticides, and herbicides (Fang and Hanna, 1999).

Currently, PLA is being used as a food packaging polymer as an alternative of commodities plastics for short shelf life products with common applications such as containers, drinking cups, sundae and salad cups, overwrap and lamination films and blister packages. Moreover, new applications include thermoformed PLA containers are being used in retail markets for fresh fruit and vegetables, since the mechanical properties of high molecular weight PLA are comparable to other commodity thermoplastics like polystyrene (PS) and poly (ethylene phthalate) (PET). PLA also possesses high transparency and is an excellent material for packaging.

As mentioned above, various advantages of PLA have been expressed, including annually renewable resources, biodegradable material, greatly benefit to environment and high mechanical properties. However, there are some limitations associated with PLA. In order for PLA to be processed on large-scale production lines in processes such as injection moulding, blow moulding, thermoforming, and extrusion, PLA must possess adequate thermal stability to prevent degradation and maintain molecular weight and properties. PLA undergoes thermal degradation at temperatures above 200 °C (Garlotta, 2001) by hydrolysis, lactide reformation, oxidative main chain scission and inter- or intra-molecular trans-esterification reactions. In packaging applications, the polymer undergoes a film extrusion process, which can be difficult due to the brittleness, thermal instability and low melt strength of PLA (Ljungberg and Wesslen, 2002). Hence, there is a need to develop polymer (or PLA) blends.

2.3 Polyhydroxybutyrate

Polyhydroxybutyrate (PHB) is a polymer in the polyhydroxyalkanoate (PHA) family which is produced from a variety of organisms. It is completely biodegradable and has suitable mechanical properties for use as a bulk polymer. It also has found use in a number of biomedical applications in part due to its biodegradability. PHB is a biopolymer that exhibits thermal properties and a tensile strength equivalent to those of petroleum-based plastics (Verlinden et al., 2007). Moreover, PHB is also biocompatible to various human tissues, and hence has been used as a biomaterial in tissue engineering.

Polyhydroxybutyrate is a thermo-plastic polyester which can be extruded and moulded on conventional processing equipment (Bucci, 2007). Moreover, due to its natural origin, PHB has stereochemical regularity and their chains are completely linear, which implies that this polymer is completely isotactic and capable of crystallizing, with a crystallinity of around 60%. Due to its high crystallinity and hydrophobic character, PHB has excellent barrier properties for use as films (Plackett, 2004). However, PHB presents some problems, such as high cost and a narrow processing window, which need to be improved. Hence, blending PHB with PLA would be beneficial as they complement each other.

2.4 Thermal Properties of PLA/PHB blends

Abdelwahab, et al (2012) presented differential scanning calorimetry (DSC) traces recorded during the second heating cycle of the PLA/PHB samples in Figure 2.2. They tested the blends with a polyester plasticizer (Lapol 108). The concentration of each polymer in blends is 75% of PLA and 25% of PHB. The curves show the glass transition temperature (T_g), cold crystallization temperature (T_{cc}) and the melting temperature (T_m). The pure PLA and PHB exhibit single peak of melting and crystallization temperatures. However, the T_g of PLA75/PHB25 shows two values which indicated that PLA/PHB blends are immiscible. The glass transition temperature of PHB is lower than that of PLA, which suggests that PHB crystallized more rapidly than PLA at low temperature.

The cold crystallization temperature (T_{cc}) of PLA doesn't change when blended with PHB, but decreases with an increasing plasticizer content. PLA75/PHB25 has higher cold crystallization temperature which is due to the small finely dispersed PHB crystals acting as nucleating agents in PLA. The one crystallization peak suggests that the PLA/PHB blends have a single homogeneous phase through the heating process. The difference in flexibility of the chains leads to the shifts in the cold crystallization peaks and shows the ability to form a crystalline structure. The two melting peaks occur in pure PLA curves are different with other presented works (Hu et al., 2008 and Zhang et al., 2010); however, the author didn't explain this phenomenon. Table 2.2 shows the degree of crystallinity (X_c) of PLA75/PHB25, which is similar with the value of pure PLA, but increases when adding Lapol (plasticizer). The increase of X_c may depend on the chain mobility of the polymer by adding plasticizer. According to Abdelwahab, et al (2012), the increase in crystallinity is due to higher chain mobility and a better packing of segments.

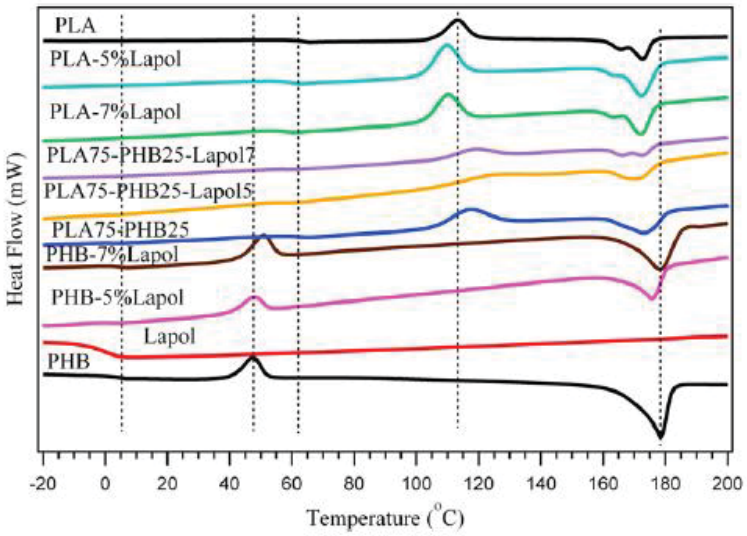


Figure 2. 2 DSC traces of the 2nd heating of PLA, PHB, Lapol and PLA-PHB-Lapol blends. (Ref: Abdelwahab et al., 2012)

Table 2. 2 DSC parameters (2nd heating) of PLA-PHB/Lapol Blends. (Ref: Abdelwahab et al., 2012)

Code	T_{g1} (°C)	T_{g2} (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} J/g	ΔH_m J/g	X_c (%)
PLA	–	63	115	173	30	33	35
Lapol	−0.7	–	–	–	–	–	–
PLA-5%Lapol	–	60	110	173	29	31	35
PLA-7%Lapol	–	58	110	172	29	31	37
PHB	5.2	–	48	179	22	72	49
PHB-5%Lapol	5.8	–	49	177	25	69	50
PHB-7%Lapol	4.6	–	50	178	25	63	48
PLA75-PHB25	1.7	62	115	173	16	13	36
PLA75-PHB25-Lapol 5	2.7	59	125	172	24	26	40
PLA75-PHB25-Lapol 7	0.6	58	120	173	24	24	38

[a] T_g, T_m are the glass crystallization and melting peak temperatures, respectively, ΔH_m is the enthalpy of melting, ΔH_{cc} is the cold crystallization enthalpy and X_c is the degree of crystallinity.

Zhang, et al (2010) reported the DSC curves of PLA/PHB blends with a heating rate of 10 °C/min, which are shown in Figure 2.3. During the first heating run, as shown in Figure 2.3(a), the recrystallization peaks of pure PLA and PHB are not apparent, however, it can be seen in PLA/PHB blends. This indicates the addition of PHB can recrystallize PLA in all blends. They suggested that there is a strong recrystallization peak in PLA75/PHB25, which

may due to the small finely dispersed PHB crystals acting as nucleating agents in PLA. The DSC curves of PLA75/PHB25 and PLA50/PHB50 show three melting peaks in the process. Zhang (2010) claimed that the lowest temperature peak corresponds to the melting of the PLA component, the next peak corresponds to the melting of the "as formed" PHB crystallites during processing and the highest peak corresponds to the melting of the PHB crystals formed from the recrystallization. They concluded that these results also indicate that PLA/PHB blends are immiscible. Figure 2.3(b) shows the cooling run, which shows crystallization peak of pure PHB, but no crystallization peak of pure PHB. It indicates that the crystallinity and crystallization rate of PHB is much higher than that of PLA, which is in agreement with the results from Abdelwahab, et al (2012). During the second heating run, Figure 2.3(c), pure PHB and PLA25/PHB75 show a double melting peak corresponding to the melting of "as-formed" PHB crystallites. Other blends and pure PLA have similar curves of the first heating run. During the second heating run, pure PHB shows a lower melting peak compared with that in the first heating run. The authors mentioned this is due to the chain scission degradation of PHB. In addition, the authors also mentioned that the improvement in thermal stability of PLA blended with PHB indicates that there is interaction between these two polymers even though the blends are immiscible.

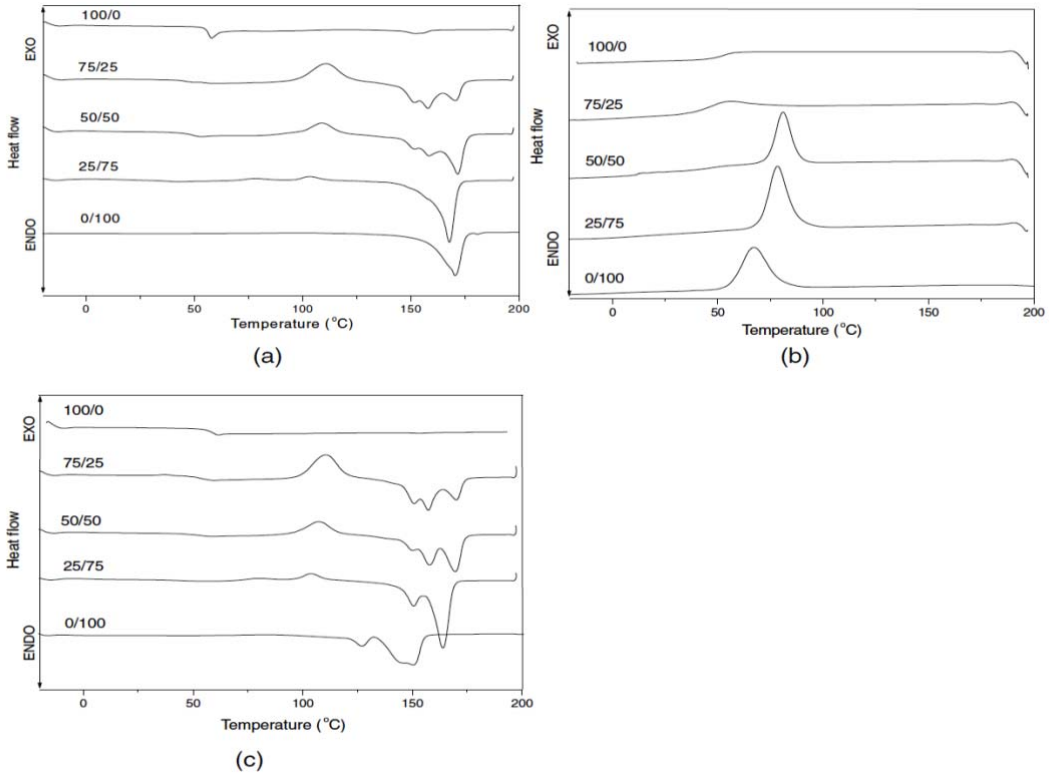


Figure 2. 3 DSC curves of PLA/PHB blends obtained from (a) first heating run, (b) cooling run, (c) second heating run. (Ref: Zhang et al., 2010)

The DSC results from Hu, et al (2008) show the difference thermal behaviours of HMW (high molecular weight)-PHB and LMW (low molecular weight)-PHB blended with PLA during the second heating cycle in Figure 2.4. In both types of blends, the cold-crystallization temperature of pure PHB is lower than that of pure PLA, which indicates that PHB crystallizes more rapidly at a lower temperature as compared with pure PLA. Hu, et al (2008) claims that molecular weight affects multiple melting behaviour of PHB, because the melting temperature of LMW-PHB was lower than that of HMW-PHB. They claimed that LMW-PHB shows some limited miscibility with PLA in PLA80/PHB20, which might be due to the cold-crystallization peak of PHB component cannot be seen in the curve, and that of PLA component shifted to lower temperature with shaper shape. Although the cold-crystallization peak of PHB component cannot be detected in HMW-PHB20/PLA80 blend either, the temperature and shape of T_{cc} (PLA component) are similar with other ratios of blends. Furthermore, compared with HMW-PHB/PLA system, T_{cc} of PLA component occur at lower temperature with higher crystallization enthalpy in LMW-PHB/PLA system.

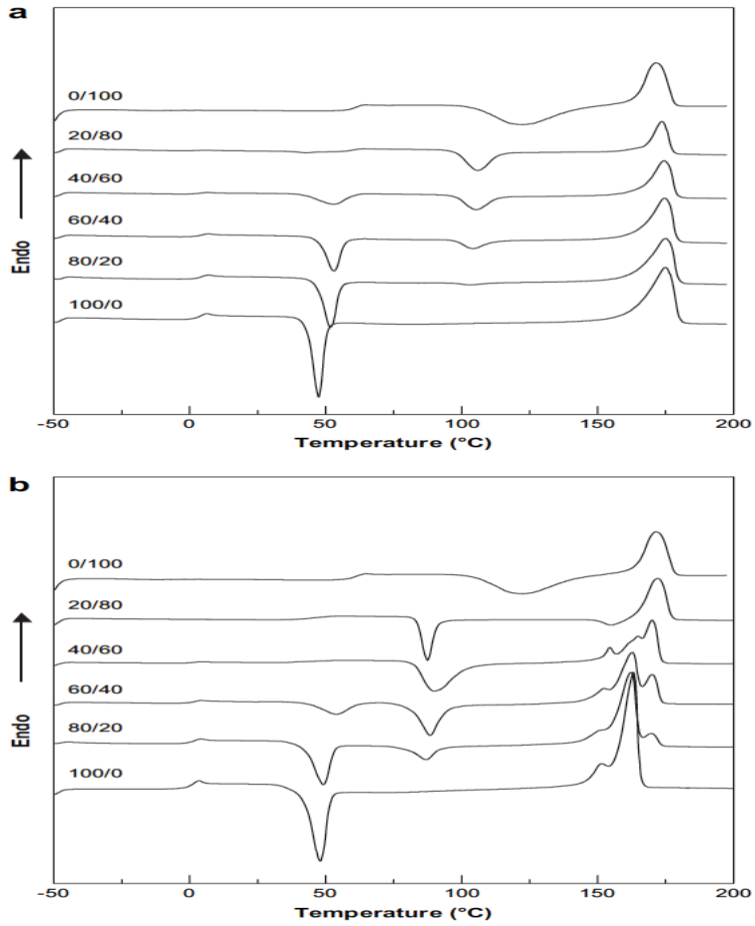


Figure 2. 4 DSC thermograms of (a) HMW-PHB/PLA blends and (b) LMW-PHB/PLA blends obtained from second heating run with a heating rate of 10 ℃/min. (Ref: Hu et al., 2008)

According to Furukawa, et al (2005), Figure 2.5 shows the DSC scans of PLA/PHB blends and pure matrix in cooling and heating processes. The crystallization peak of PHB is observed for PHB60/PLA40 and PHB80/PLA20 blends, but cannot be seen in PHB40/PLA60 and PHB20/PLA80 blends. This indicates PHB doesn't crystallize much in the blends containing lower PHB content during cooling process.

In the heating cycle, the blends with higher content of PHB and pure PHB show double peaks of melting temperature, which is caused by the melting and subsequent recrystallization of PHB. The recrystallization peak only shows in pure PLA and PHB20/PLA80 in heating cycle, which means that only PHB20/PLA80 can recrystallize PLA component. Moreover, the recrystallization temperature of PHB20/PLA80 is lower than that of pure PLA which suggests that the non-isothermal crystallization rate of PLA in

PHB20/PLA80 is faster than that of pure PLA. This indicates that PHB forms small finely dispersed crystals and act as nucleation sites of PLA. On the other hand, PLA is not crystallized in blends containing high content of PHB

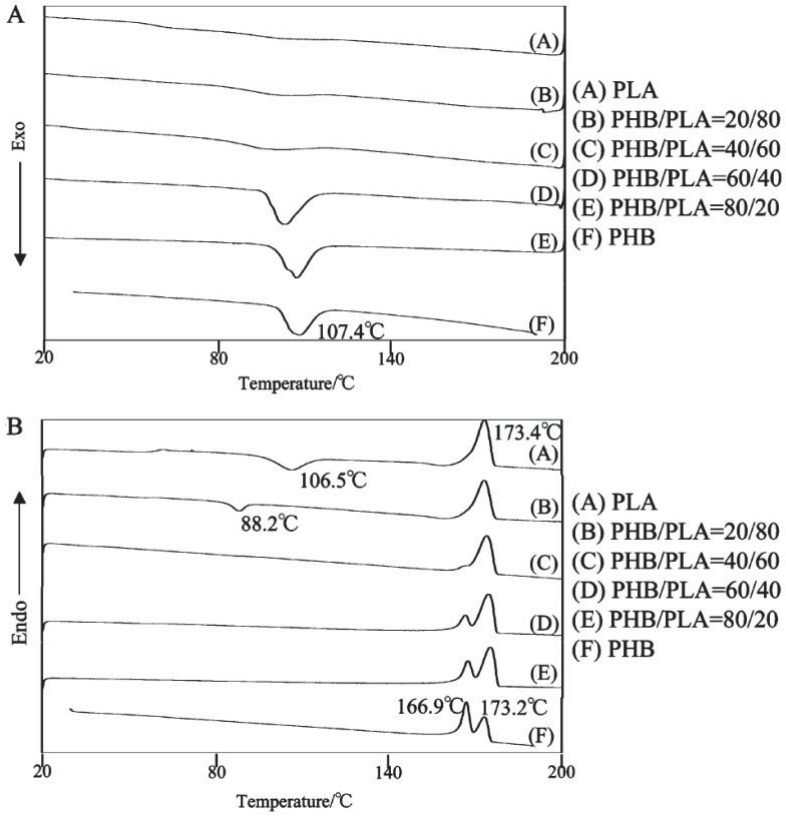


Figure 2. 5 DSC scans during the cooling and heating processes of PHB, PLA and the four kinds PHB/PLA blends: (A) cooling process, (B) heating process. (Ref: Furukawa et al., 2005)

2.5 Rheological Properties of PLA/PHB Blends

For the rheological results from Modi (2003), they tested three different grades of PLA (3051D, 4042D and 6202D) blended with PHBV with 5% HV content (T5) (from Tianan Biologic Material Co.). Figures 2.6(B) and 2.7(B) show T5 blended with PLA 4042D at 160 °C and 170℃. At 160 °C, the viscosity doesn't change as PHBV content is increased, while the pure PHBV has highest complex viscosity in whole frequency range. However, the viscosity of blends increase as PHB content is increased, but the PHB70/PLA30 shows the lowest value. As the decreasing viscosity of PHB60/PLA40, Modi (2003) suggested that cleavage of the polymer chains lead to decreasing viscosity.

The authors showed the dynamic storage modulus (G') and loss modulus (G") at 160 °C and 170 °C in Figures 2.8 and 2.9, respectively. At 160 ℃, pure PHB (denoted as T5%) shows a more solid-like behavior compared to pure PLA (3051D). They mentioned that the blends possess liquid-like structures in which G" is higher than G' throughout the frequency range. Moreover, the storage moduli of all blends show frequency-independent behaviour at 160 °C, except pure PLA. The G' and G" values decease with increasing PHB concentration of the PLA/PHB blends.

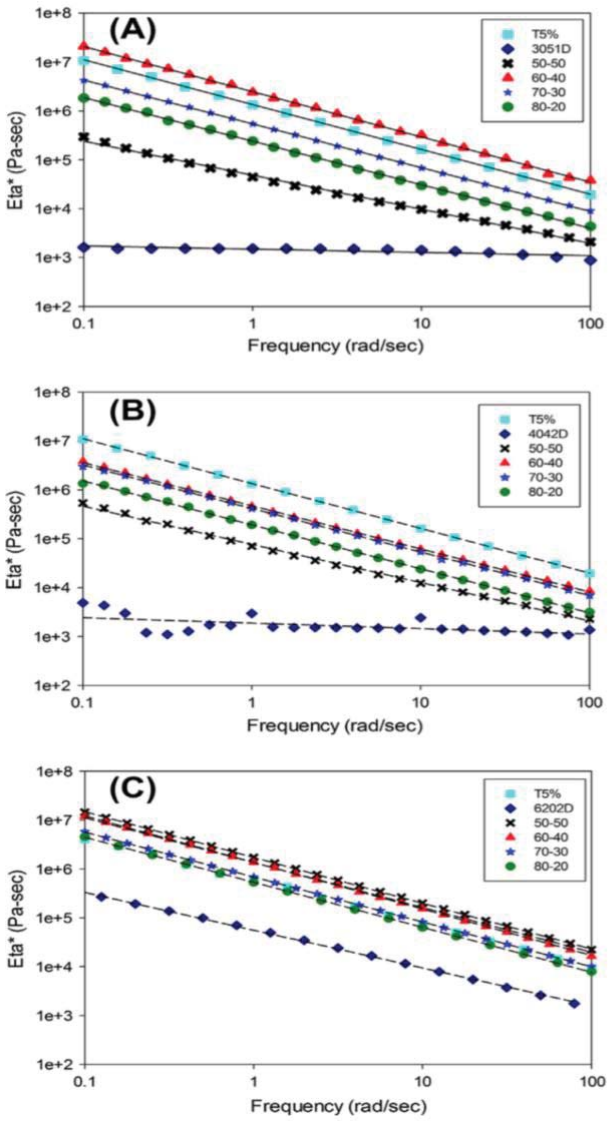


Figure 2. 6 Complex viscosity curves of various blends (T=160 °C) as a function of oscillatory frequency and the Power-law data fit curves. (A) for T5-3051D, (B) for T5-4042D, (C) for T5-6062D. (Ref: Modi et al., 2003).

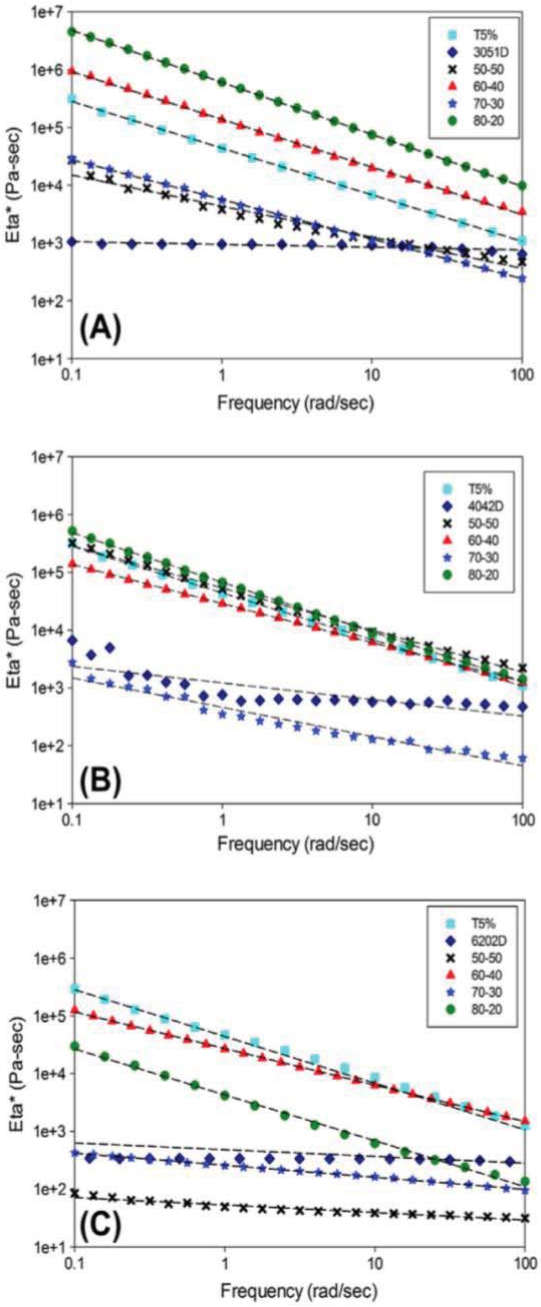


Figure 2. 7 Complex viscosity curves of various blends (T=170 °C) as a function of oscillatory frequency and the Power-law data fit curves. (A) for T5-3051D, (B) for T5-4042D, (C) for T5-6202D. (Ref: Modi et al., 2003)

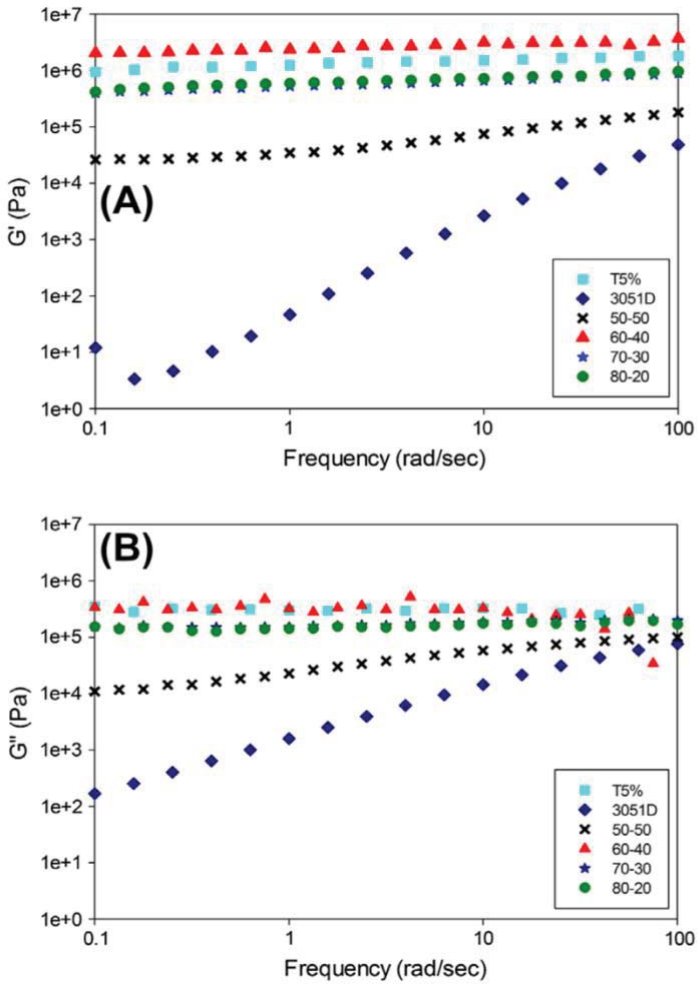


Figure 2. 8 Dynamic frequency curves of various blends (T=160 °C) for the Tianan PHB (T5) blended with PLA (3051D). (A) for Dynamic storage modulus (G') and (B) for loss modulus(G''). (Ref: Modi et al., 2003)

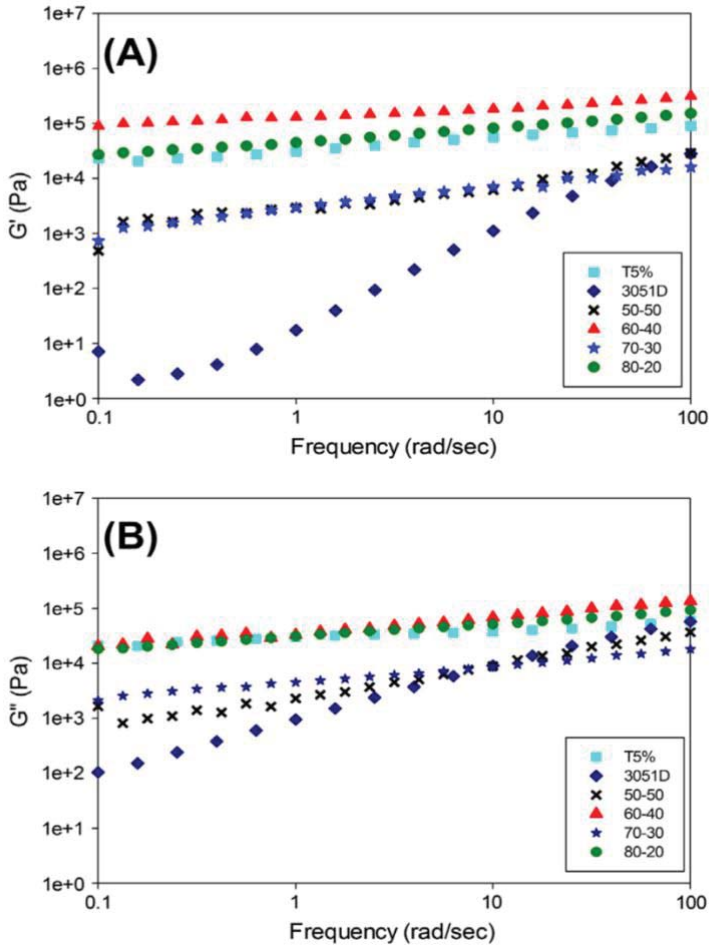


Figure 2. 9 Dynamic frequency curves of various blends (T=170 °C) for the Tianan PHB (T5) blended with PLA (3051D). (A) for Dynamic storage modulus (G') and (B) for loss modulus(G''). (Ref: Modi et al., 2003)

Aluthge et al., (2013) presented master curves of the linear viscoelastic modulus (G' and G") and complex viscosity of the triblock copolymers (PLLA-PHB-PDLA) with different PHB content in the temperature range of 180 °C to 200 °C (Figure 2.10). The loss modulus is higher than the storage modulus for the whole frequency range, which indicates a liquid-like behaviour of the blends; this is in agreement with the results reported by Modi (2013). Moreover, the author claims that triblocks with PLLA and PDLA form stereocomplex crystallites which impact the rheological properties. Adding PHB as the middle block changes the rheological properties of the triblocks, which shows more elastomeric (solid-like behaviour) (Figure 2.11).

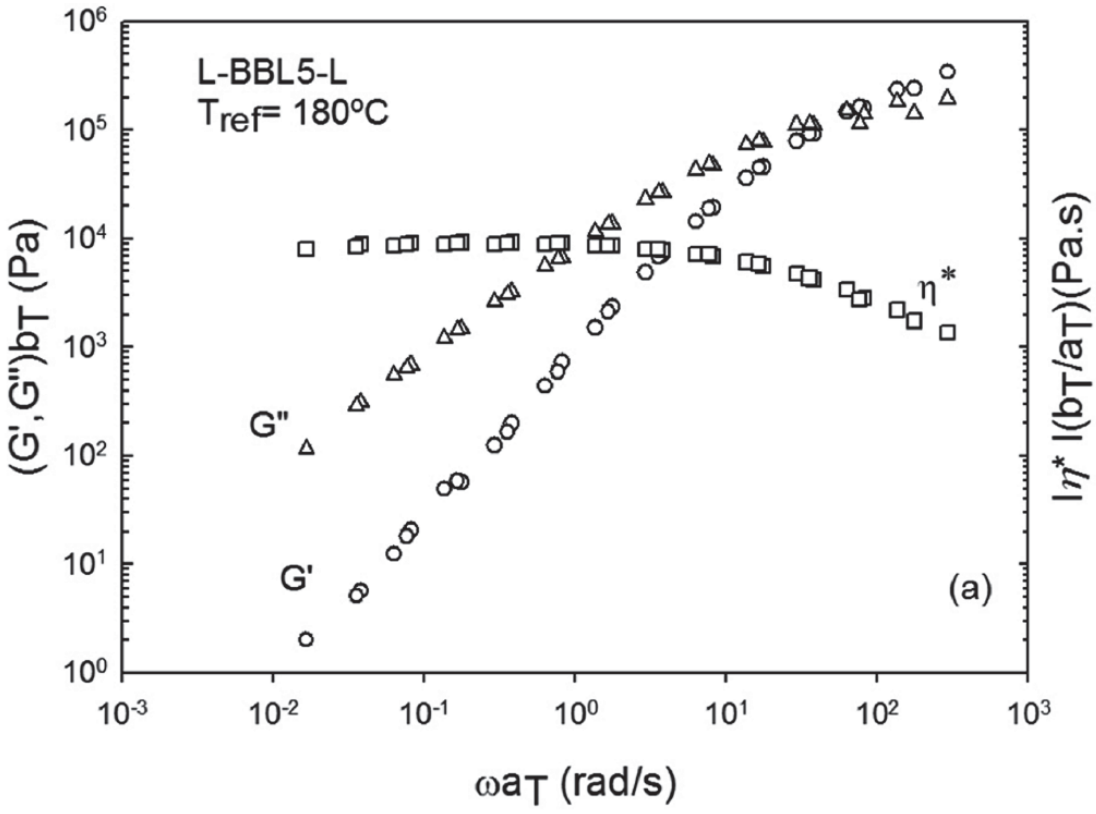


Figure 2. 10 Master curves of the linear viscoelastic modulus (G' and G") and complex viscosity (Eta*) of PLLA47-PHB5-PLLA47 at the reference temperature of 180 °C. (Ref: Aluthge et al., 2013)

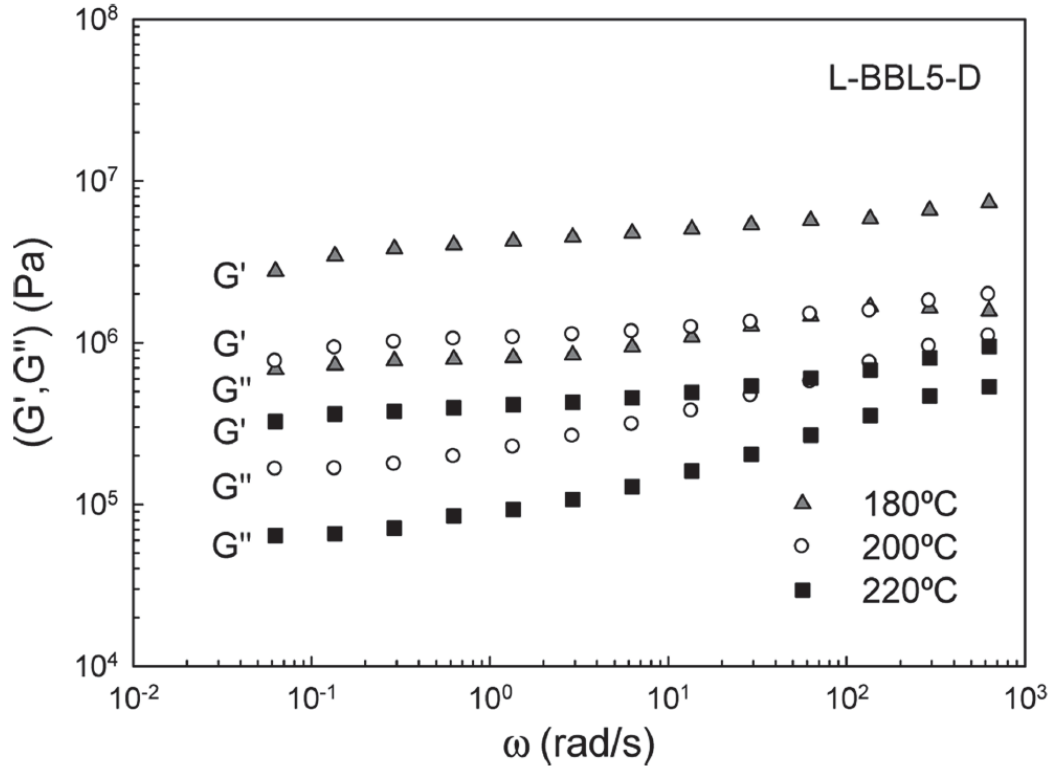


Figure 2. 11 G' and G" of copolymer PLLA47-PHB5-PDLA47 at 180 °C, 190 °C and 200 °C. (Ref: Aluthge et al., 2013)

Micic (1997) investigated the effect on rheological properties of LLDPE/LDPE blends (shown here in Figures 2.12 and 2.13). Their results show blends exhibit larger values of the complex viscosity and storage modulus than pure matrix, which indicates the synergistic behaviour for the LDPE rich blends. According to Micic (1997), the synergistic region is referred to as a region where the rheological properties for blends have a higher value than the pure one. Moreover, as the temperature decreases the synergism in the complex viscosity and storage modulus values becomes more significant. The synergistic behaviour of the rheological properties is due to the larger level of interactions existing in blends than in pure polymers. The authors said that the enhanced level of interactions in blends was due to the stronger nature of entanglement coupling between the different macromolecules of LLDPE and LDPE.

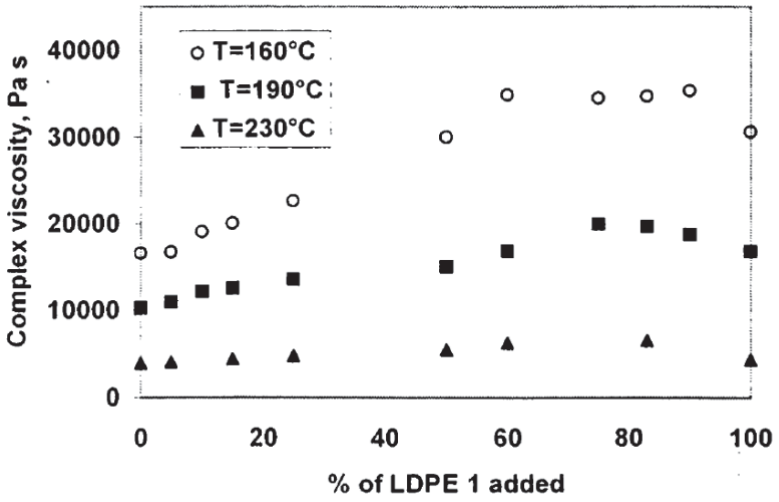


Figure 2. 12 Complex viscosity of LLDPE/LDPE 1 blends at different temperatures. (Ref: Micic, 1997)

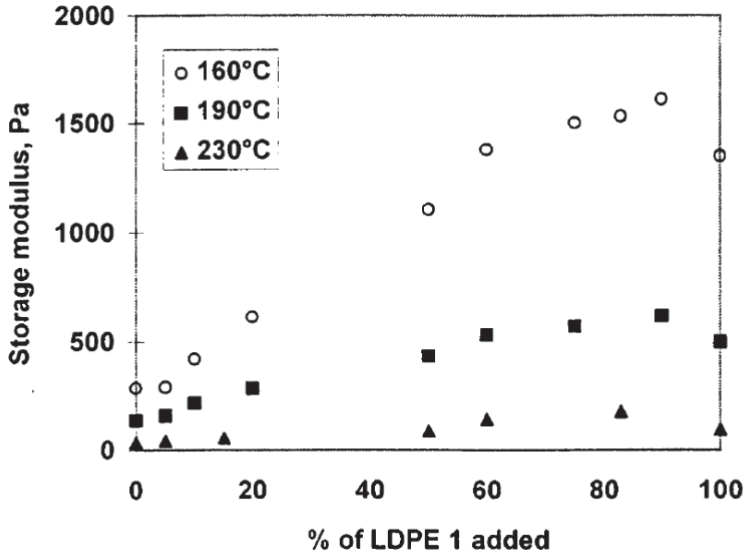


Figure 2. 13 Storage modulus of LLDPE/LDPE 1 blends at different temperatures. (Ref: Micic, 1997)

Micic (1997) also claimed that the independence of storage modulus and loss modulus to blend composition could assume the blends are miscible (Figure 2.14). The G' and G" of PLA/PHB blends don't follow the same line as changing the composition. They concluded

that these results justify the assumption about the compositional dependence of the G' versus G" plot for immiscible systems.

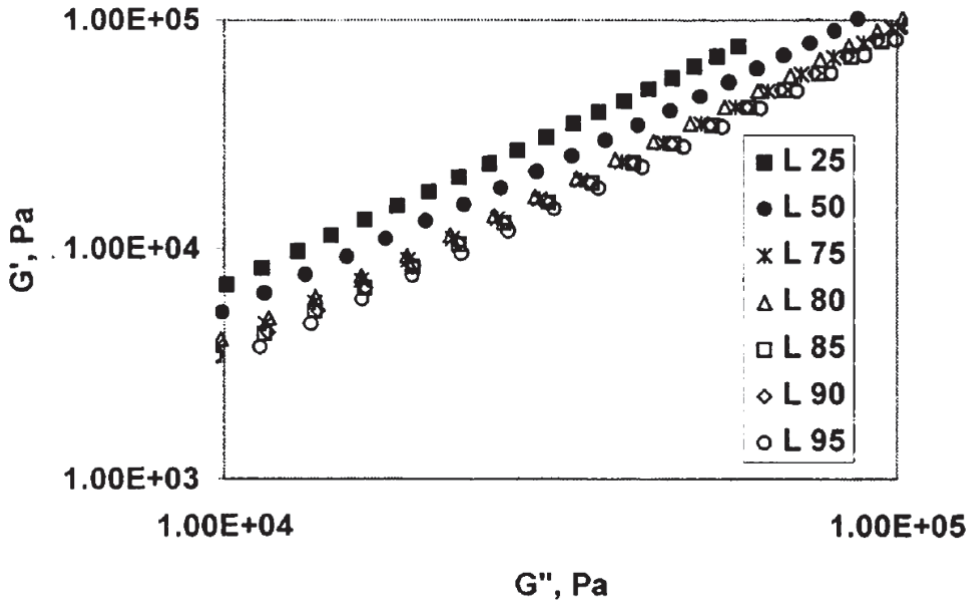


Figure 2. 14 G' versus G" for LLDPE/LDPE blends at 190 °C. (Ref: Micic, 1997)

Chapter 3 Materials and Equipment

This chapter describes the materials and equipment used in this research. In addition, it also illustrates the experimental methodologies including samples fabrication techniques used to prepare PLA/PHB blends as well as characterization techniques (mainly dynamic rheological and thermal properties measurements).

3.1 Materials

Grade 4032D Polylactic acid was supplied by Nature Works LLC with a density of 1.24 g/cm^3 and a melting point about 160 °C was chosen as matrix. Polyhydroxybutyrate (PHB) was supplied as powder by Sigma-Aldrich (Australia), product number: Aldrich-363502, with an average molecular weight (M_w) of 425 KDa and polydispersity of 2.51. The physical properties of PLA and PHB, as presented in Table 3.1, were obtained from the suppliers, except some values with* were obtained from literature.

Table 3. 1 Physical properties of PLA and PHB

Properties	**PLA**	**PHB**
T_m (°C)	150-162	171-182
T_g (°C)	45-60	5-15
ρ (g/cm^3)	1.21-1.25	1.23-1.25*
σ (Mpa)	21-60	40*
E (Gpa)	0.35-3.5	3.5-4*
ϵ (%)	2.5-6	5-8*

*** Values obtained from literature**

3.2 Samples Preparation

Both of PLA and PHB were prepared by drying at 85 °C for 8 h to eliminate possible absorbed water on the surface of the particles. Measured quantities of each polymer were first mixed in a container before blending in a Haake Rheomix OS R600 internal mixer. The mixer was operated at 180 °C, 50 rpm screw speed and 5 minutes for producing all blends. A total of 50 g material was fed into the mixer for every batch. Blends were prepared at twelve different PHB concentrations from 0 to 100 wt% in 10 wt% increments. Table 3.2 summarizes the compositions of the sample and their corresponding codes.

Table 3. 2 Compositions of PLA/PHB blends

Sample codes	**PLA100/PHB0**	**PLA90/PHB10**	**PLA80/PHB20**	**PLA75/PHB25**	**PLA70/PHB30**	**PLA60/PHB40**	**PLA50/PHB50**	**PLA40/PHB60**	**PLA30/PHB70**	**PLA20/PHB80**	**PLA10/PHB90**	**PLA0/PHB100**
PLA (wt%)	100	90	80	75	70	60	50	40	30	20	10	0
PHB (wt%)	0	10	20	25	30	40	50	60	70	80	90	100

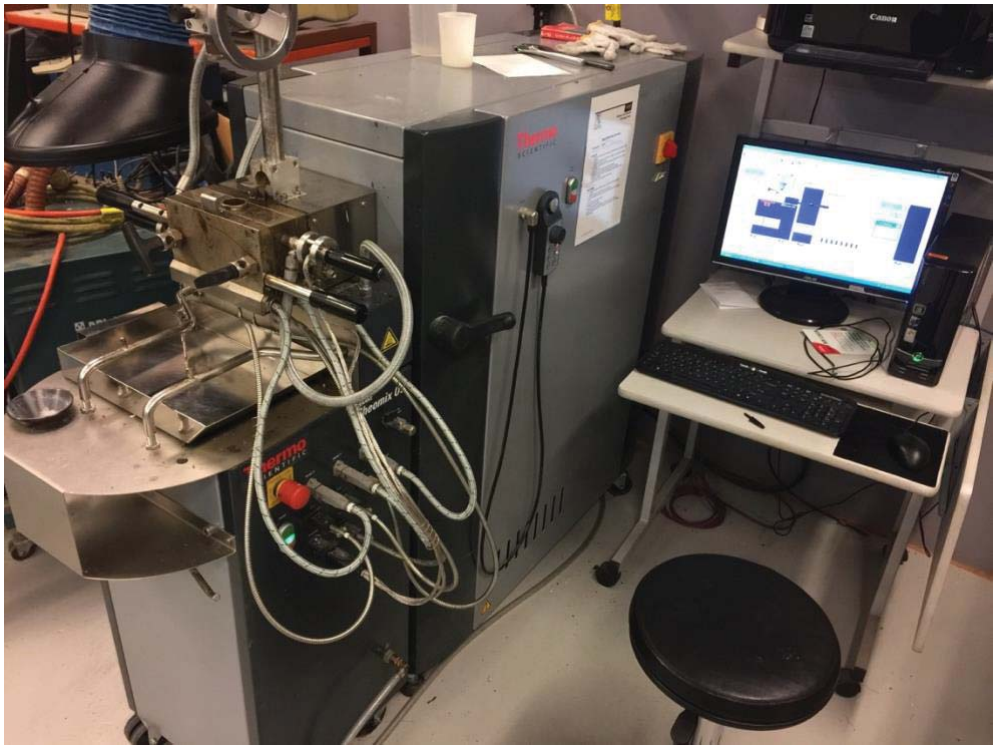


Figure 3. 1 Haake Rheomix OS R600 internal mixer

3.3 Modulated Differential Scanning Calorimetry (MDSC)

Modulated differential scanning calorimetry (MDSC) is a thermo-analytical tool used to study the thermal transitions based on chemical or physical characteristics. The technique involves heating of a sample and a reference pan at the same rate over a specific temperature range. The heat differential that is formed by increasing the temperature is measured and plotted as a function of temperature. When the sample undergoes a physical transformation, the process is either exothermic or endothermic and is displayed as a MDSC thermogram. From the curve, the heat capacities, melt enthalpies, transition temperatures, and chemical reactions can be measured and can provide information regarding crystallization and phase transitions.

In this work, MDSC tests were carried out in a modulated DSC mode on the TA Instrument Model 2920 (Figure 3.2). Sealed aluminium pans containing 5-10 mg of PLA/PHB blend samples were used in all experiments. The samples were preliminarily heated to 190 °C to discard any anterior thermal history and held at that temperature for 2 min. It was then brought to -20 °C and kept at -20 °C for 5 min before heating from -20 °C to 190°C at

2 °C/min scan rate and kept at that temperature for another 2 min. Finally, the sample was cooled to -20 °C at a rate of 2 °C/min and kept at -20 °C for 10 min. During the procedure, the glass transition (T_g), cold crystallization (T_{cc}) and melting temperature (T_m) of the material could be determined, and the crystallization temperature was determined from the cooling scan.

The glass transition temperature or melting temperature of a polymer blend gives an indication on the miscibility of the material. A single T_g or T_m implies miscibility between the components. If the T_g of the blends is lower than the T_g of the brittleness or stiffness component as pure material, it means that the blends have more flexible chains which can reduce the stiffness and improving processability. Two or more T_g or T_m indicate immiscibility. However, this doesn't mean that there are no interactions between the components.

Figure 3. 2 TA Instrument Model 2920

3.4 Rheology test

Rheology is defined as the study of the deformation and flow of a fluid. Some of the important properties of molten polymers are storage and loss moduli and the dependence of the viscosity on temperature. Moreover, the shear thinning behaviour of polymer is due to

the decreasing of the polymer molecules orientation and the number of entanglements between the polymer chains, which make it easier for the chains to flow past one another. And also, the viscosity decreases with increasing temperature because of the increase in the kinetic energy of the molecules. To understand the rheological behaviour, a rigorous study should be performed on polymer materials. Rheological measurements in general are well established as laboratory methods to characterize polymers with respect to processing.

Rheological measurements were carried out on the Advanced Rheometrics Expansion System (ARES) rheometer (Figure 3.6). Samples required for rheological measurements were compression-moulded (Figure 3.3) at 10 MPa for 5 minutes using a circular plaque, followed by cooling with cooling water to room temperature under a constant pressure of 10 MPa. The moulded samples (parallel plate) (Figure 3.4) are of 25 mm diameter and a thickness of between 1.6 and 2.0 mm.

Figure 3. 3 Compression moulded machine

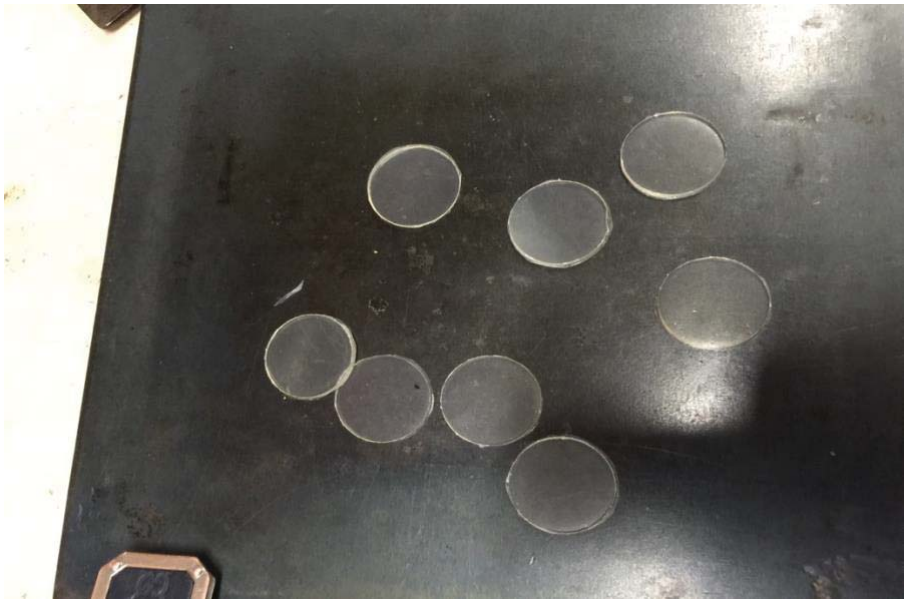


Figure 3. 4 The prepared sample circular plaques (parallel plate).

The following tests were performed:

(a) Dynamic rheological experiments at a same gap between two plateaus as 1.8 mm.

(b) Dynamic strain sweep experiments to assess the limits of linear viscoelastic property at various frequencies

(c) Dynamic frequency sweep experiments at a fixed strain value over a frequency range of 0.1-100 rad/s.

The linear viscoelastic response of blends was determined by measuring their storage modulus (G') and loss modulus (G") at 180 °C at 1 rad/s frequency to determine the linear viscoelastic region. The results of the linear viscoelastic region of the blends at other frequencies (0.1, 10 and 100 rad/s) showed similar behaviour. Frequency sweeps at 10 % strain were then conducted on fresh samples within their linear viscoelastic region to determine the effect of PHB concentration on storage and loss moduli and also dynamic viscosity of PLA/PHB blends at 3 different temperatures (180, 190, and 200 °C).

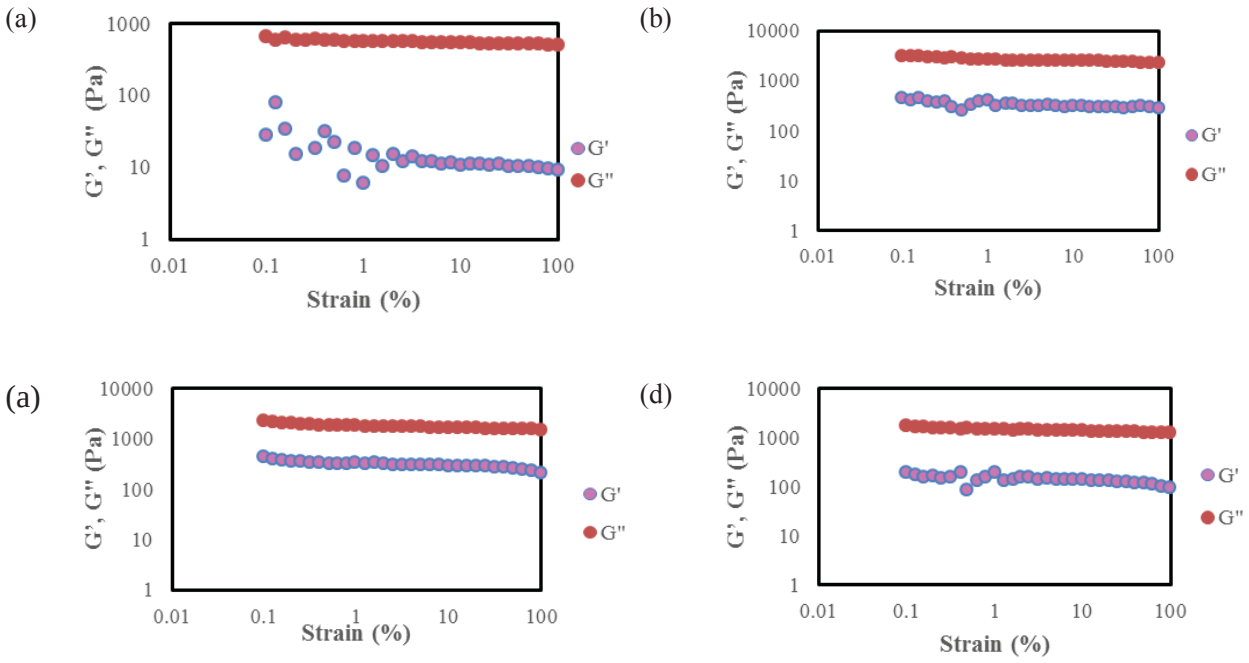


Figure 3. 5 Dynamic strain sweep in different concentration of the PLA/PHB blends at 1 rad/s frequency: (a) PLA100/PHB0 (b) PLA90/PHB10 (c) PLA75/PHB25 (d) PLA60/PHB40

Figure 3. 6 Advanced Rheometrics Expansion System (ARES) rheometer

3.5 Error analysis

According to Sungsanit (2011), an experimenter may encounter one or more types of errors while conducting an experiment: human error, systematic error, and random error.

- **Human error** happens when human make mistakes during experimental processing. It may occur when researchers set up the experiment in incorrect way, or data calculation is mistakenly done. Human errors are not a kind of experimental error, so that it should be not correct, if people compare the human error with experimental error.
- **Systematic error** is a kind of errors of the experimental device which is inherent. It may make the experimental results shifting in the same direction every time. Sometimes, systematic errors can be corrected easily. However, researchers also

may use different experimental devices or setup to eliminate some systematic errors.

- **Random error** can cause a series of measurements which because no measurement can be carried out indefinitely. The random error can be reduced by means of average measurement.

Therefore, one of the methods to analyse the experimental error is the percentage (%) error calculation. It is not easy to avoid errors in the preparation of the sample or in the process of experimental measurements. These errors will affect the nature and conclusion of the experimental work. The purpose of this section is to briefly discuss the errors associated with experimental measurements conducted in this research.

Errors Analysis of Rheological Measurement

The errors associated with rheological measurements could be generated from systematic error, random error and human error. Random error included variable nature of the PLA and PHB polymers and its properties such as degradation due to high temperature. Systematic error includes temperature control of the machine used for rheological measurements. Human error was observed during the loading of the sample between plates and setting up minimum gap between the plates.

All samples tested were carefully prepared to ensure that they were bubbles free. Any samples with bubbles were not tested.

Figure 3.7 shows the thermal degradation of the pure PHB samples at 200 °C. It was very difficult to avoid thermal degradation of the sample at very high temperature although nitrogen atmosphere was used to avoid thermal degradation of the sample. Thermal degradation of the samples subjected to elevated temperatures for a long time can have adverse effect on their microstructure. Changes in microstructure can lead to chain scission and cross-linking or other physical-chemical process that can adversely affect the material properties.

Figure 3. 7 Pure PHB sample outflow from plateau during test at 200 °C.

To avoid the influence of systematic, human and random errors of experimental data, all data collection processing was repeated at least three times or more. Figure 3.8 shows the reproducibility of Pure PLA (i.e. PLA100/PHB0) sample by comparing repeated measurements of fresh samples 5 times and comparing them with my research colleagues' results. As can be seen, the reproducibility of these experiments was excellent and this behaviour has been observed for all samples tested as well.

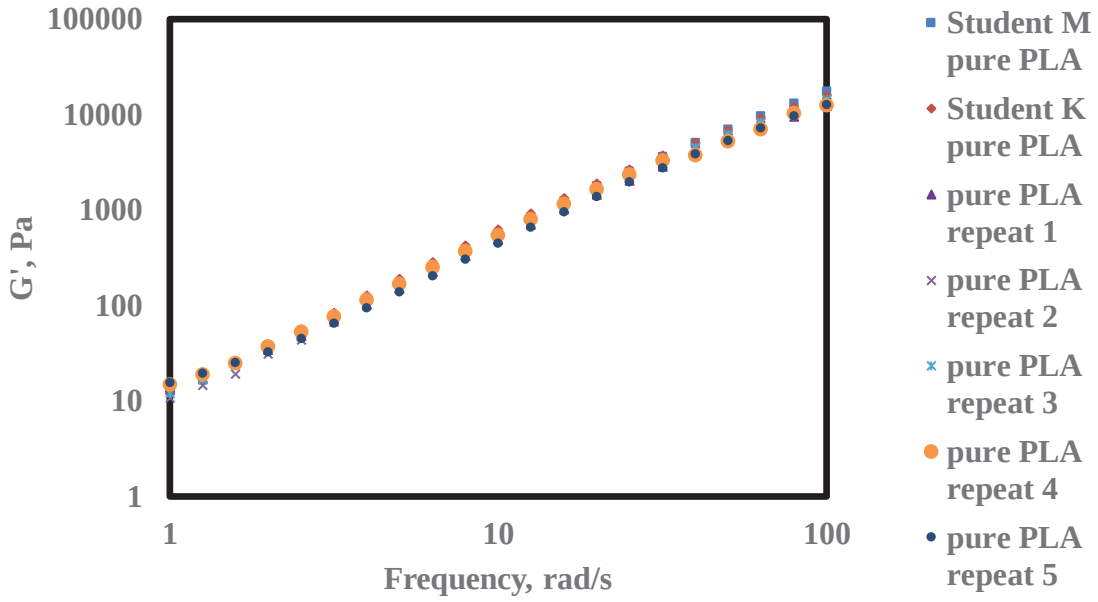


Figure 3.8 Reproducibility of PLA100/PHB0 results

Error Analysis of MDSC

The main source of error in MDSC measurements came from the small size of the samples (5-10 mg) and loading the small sample into sealed aluminium pans before the thermal processing. This error could be minimized by averaging the weight of the samples. The second error in this characterization technique is the thermal history of the samples. To discard any anterior thermal history, the samples were preliminarily heated to 190 °C and held at that temperature for 2 min.

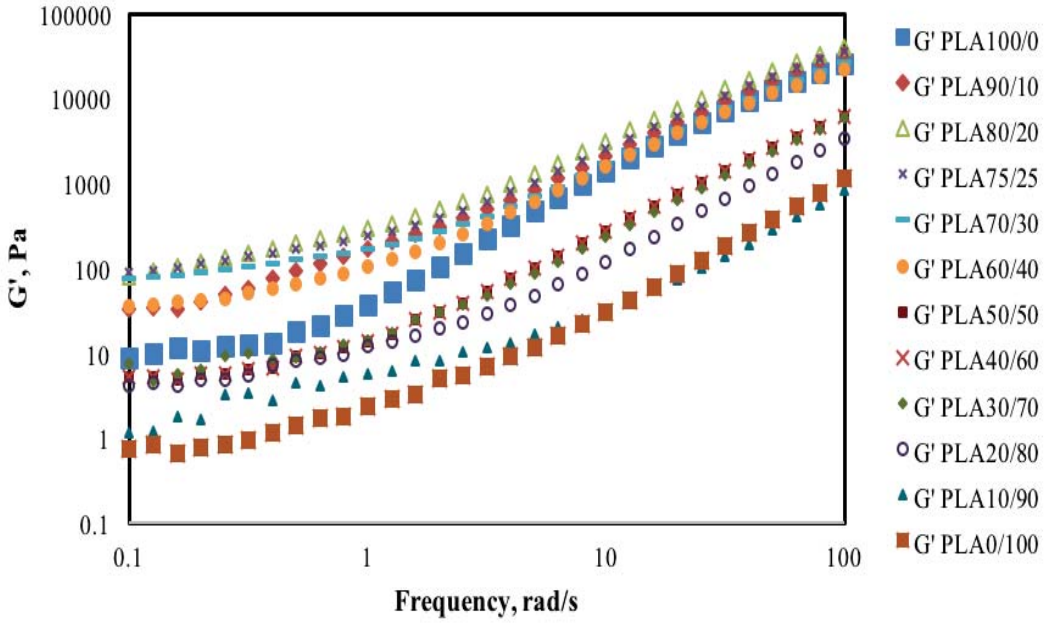
Chapter 4 Properties of PLA/PHB Blends

In this chapter, the rheological properties of PLA/PHB blends based on different concentration are presented. The dynamic modulus and viscosities comparison are presented and discussed as determined through the rheology experiments. And also, the storage and loss moduli, dynamic viscosities, mixing rule and Time-Temperature Superposition (TTS) which based on different concentration of PLA/PHB blends are presented. Moreover, the glass transition, melting, cold crystallization temperature and crystallinity of the thermal properties of PLA/PHB blends based on different concentration are explained as determined through the experiments.

4.1 The Effect of Concentration on the Rheological Properties of PLA/PHB Blends

Storage modulus (G') is an important parameter in characterizing the viscoelasticity of polymer melts; it describes the ability of storing elastic deformation energy of the melts. Loss modulus (G") is also an important parameter in characterizing the viscoelasticity of polymers melts as well; it describes the phenomenon when energy dissipation is changed as heat in the case of the deformation of the polymer melts. The storage modulus and loss modulus of pure PLA, pure PHB, and their blends at 180 °C are shown in Figure 4.1. The storage modulus and loss modulus with a frequency range from 0.1 to 100 rad/s was measured for each blend within the linear viscoelastic region (at 10% strain). According to Ngai et al., (2013), the effect flow field on polymer melts would be enhanced with increasing frequency, both the deformation and the viscous dissipation of deformation energy would increase correspondingly. As a result, the loss modulus would increase with increasing frequency.

(a)



(b)

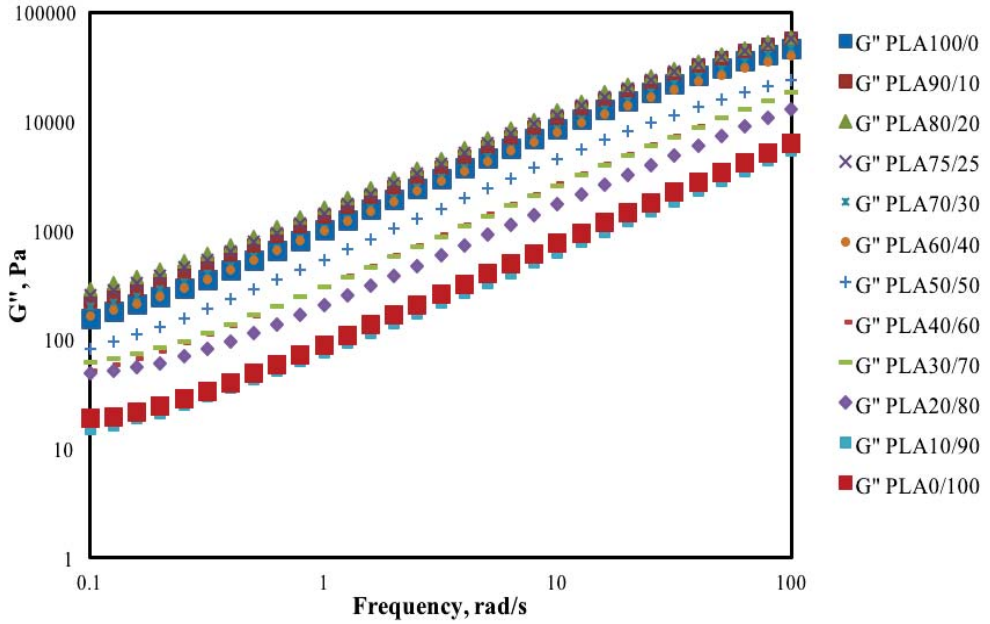


Figure 4. 1 Comparison Storage modulus (G'), loss modulus (G") of PLA/PHB blends at different concentration at 180 °C.

It could be observed that the storage and loss moduli of PLA/PHB blends were frequency-dependent. Blends in which PLA was the major component showed significantly greater G' and G" than blends in which PHB was the major component, except the pure PLA. The results showed that G' and G" values of the blends increased significantly with increasing PHB content, especially at the low frequency region (< 1rad/s). The G' and G" of the PLA80/PHB20 blend showed the highest values over the whole frequency range tested (0.1-100 rad/s). On the other hand, the PLA0/PHB100 (i.e. pure PHB) showed the lowest G' and G" over the whole frequency range covered. The PLA blends samples, showed a gradual deviation from the terminal liquid-like behaviour to a solid-like behaviour with increasing PHB content (less than 50 wt%), as evidenced by the decrease in the slope of G' at low frequency region (0.1-1 rad/s). Moreover, the high G' at low frequency may be due to the reason that the blends behaved like solid at low frequency and as a liquid at high frequency. The PLA blends samples showed a higher elasticity with increasing PHB content (less than 50 wt%). The storage and loss moduli of blends containing high content of PHB (50-90 wt%) were lower than pure PLA, but higher than pure PHB, and also increased with decreasing PHB concentration. This indicated that there was no strong molecular interaction between PLA and PHB as the blends were immiscible and also the inadequate dispersion of high PHB content (Zhang et al., 1995, Zhang et al., 2010). However, adding PLA into PHB could decrease the crystallinity of PHB as well, which may have led to the increasing modulus. PHB formed large crystals that did not act as efficient nucleation sites for PLA at high content. On the other hand, blends containing high PLA content (60-90 wt%) exhibited molecular interactions due to the finely dispersed PHB crystals acting as filler and nucleating agent in PLA. The storage modulus finally declined as they were influence by the interactions between the amorphous and the crystalline regions of the PLA.

Figure 4.2 shows the dynamic viscosity (η') of the PLA/PHB blends at 180 ℃. Similar to the storage and loss moduli results, blends in which PLA was the major component exhibited significantly greater η' than blends in which PHB was the major component, except the pure PLA. The results showed that the η' value of the blends increased significantly with increasing PHB content (less than 50 wt%). In contrast, all blends exhibited a Newtonian plateau in the low frequency range (1-10 rad/s). The shear thinning was more prominent at higher frequency range (>10 rad/s) due to the disentanglement of the polymer chains, which led to an increased movement and subsequently lowered the dynamic viscosity. But at higher frequency, blends with the lower PHB content shear thinned stronger than blends with the

higher PHB content. This could be due to the interactions between the two polymers at low content of PHB. The PLA80/PHB20 blend showed the highest dynamic viscosity value over the frequency range tested. The blends showed slightly Newtonian-like behaviour at higher PHB content as decreasing in slope over the shear thinning region values.

Nitin (2006) indicated that the decrease in viscosity, known as pseudoplastic behaviour, occurs as the polymer chains are aligned and disentangled in the direction of the melt flow. The polymer chains break at higher frequency range.

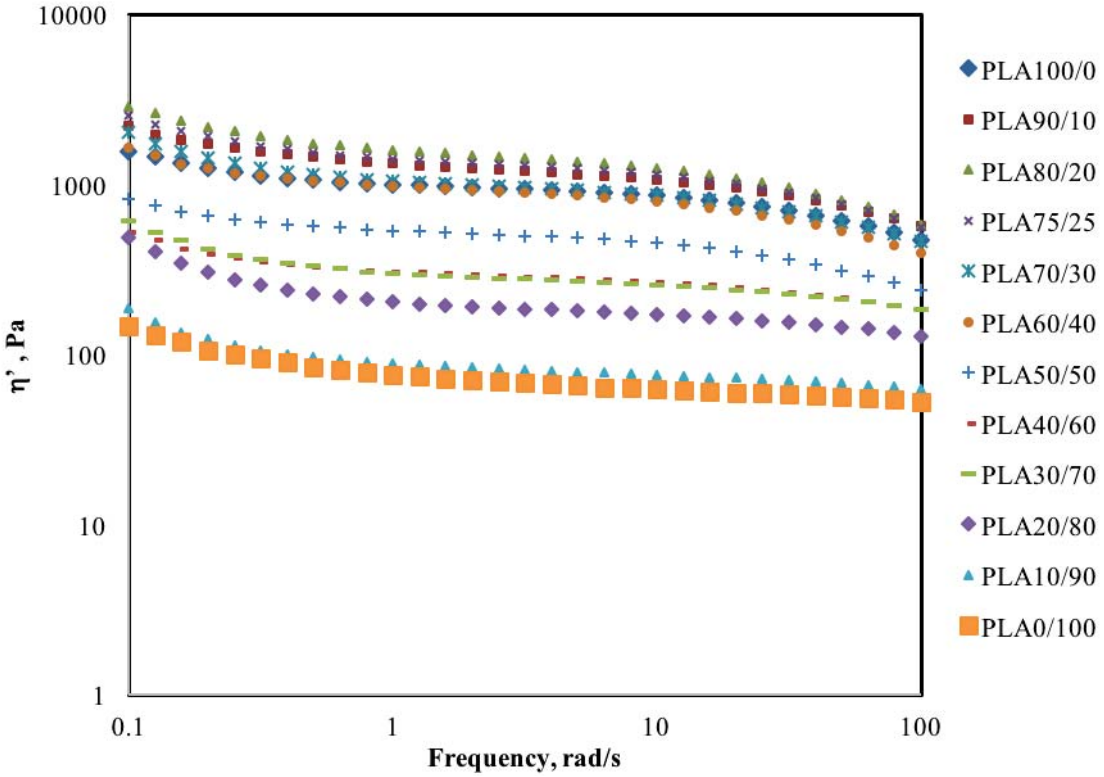


Figure 4. 2 Comparison of Dynamic viscosity (η') of PLA/PHB blends at different concentrations at 180 °C.

Figure 4.3 illustrates the relationship between the storage modulus, loss modulus and dynamic viscosity of the PLA/PHB blends at different PHB content at 0.1 rad/s. It was found that the value of G', G", and η' increased with an addition of the PHB weight fraction from 0 to 20 wt%, after which they decreased drastically over the 20-60 wt% PHB concentration range and then gradually over the 60-100 wt% PHB concentration range. It could be

concluded that the PLA/PHB blends containing 20-25 wt% PHB possessed the optimum concentration in terms of the rheological properties of PLA/PHB blends.

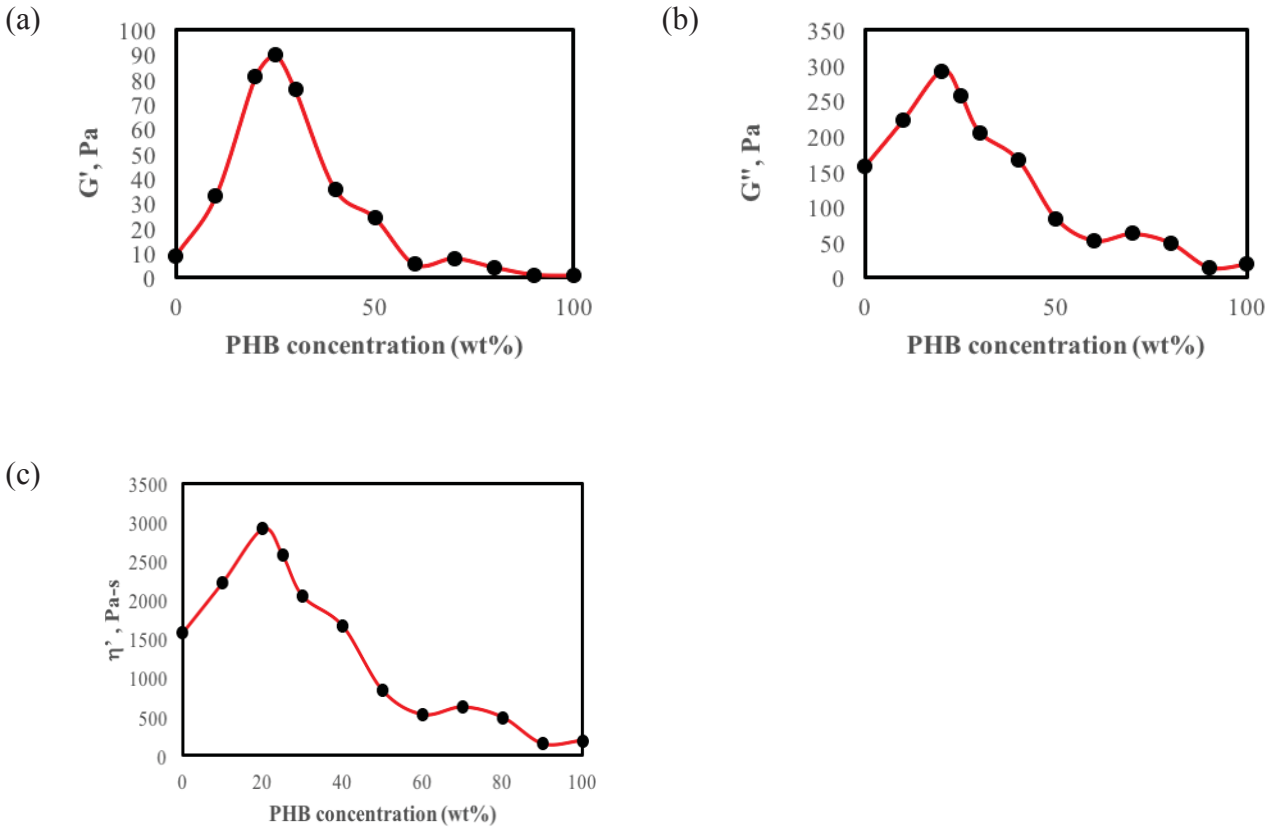


Figure 4. 3 Comparison of G', G", and η' results of PLA/PHB blends at 180 °C and 0.1 rad/s.

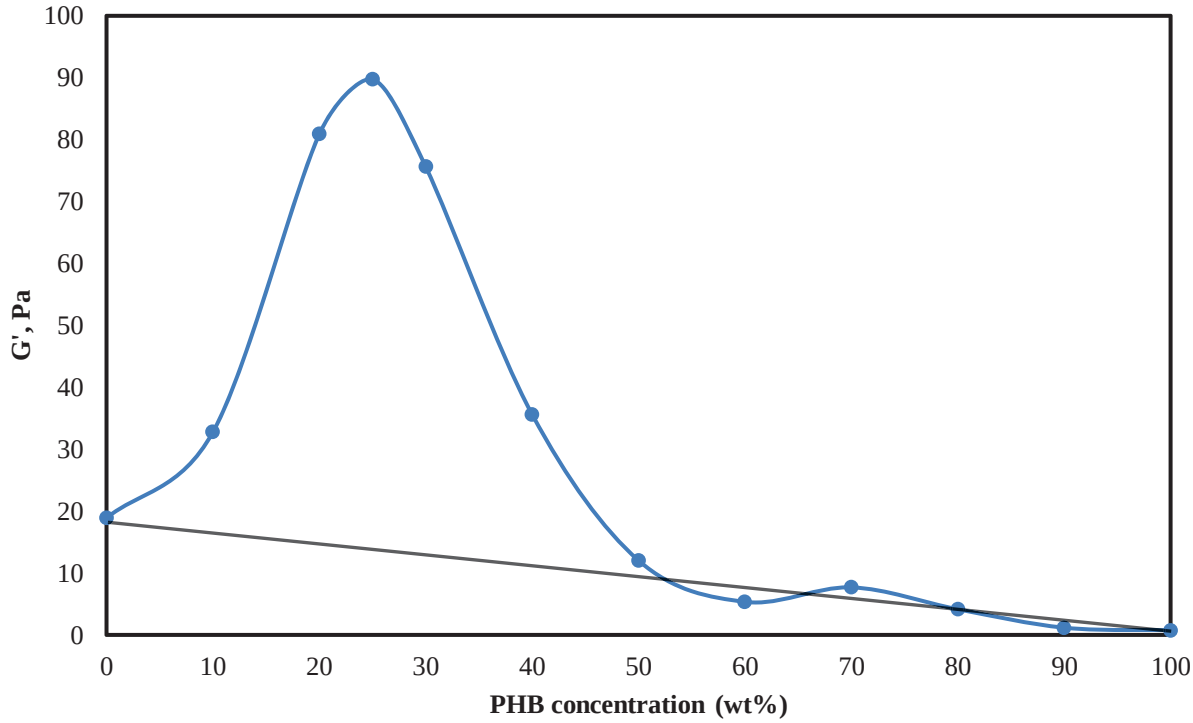


Figure 4. 4 Mixing rule of G' at 180 °C (Frequency = 0.1 rad/s).

Figure 4.4 shows the mixing rule, as indicated by the solid line, of G' at 180 °C at 0.1rad/s. Other two temperature curves exhibited similar manner. The results showed a positive deviation (behaviour) for PLA100/PHB0 to PLA50/PHB50 blends in which the G' values were above the mixing rule line. As the PHB concentration was increased from 60-100 wt%, G' values remained almost on the mixing rule line (within experimental errors).

It can be concluded from the above results that the optimum PLA/PHB blends occurred at 20-25 wt% PHB content.

4.2 The Effect of Temperature on the Rheological Properties of PLA/PHB Blends

The Figure 4.5 shows the comparison G' and G" of PLA80/PHB20 blends at 180 °C, 190 °C and 200 °C. The PLA/PHB blends exhibited a normal temperature dependent where G'(filled symbols) continuously decreased with increasing temperatures. The loss modulus (unfilled symbols) values of the PLA/PHB blends demonstrated temperature dependency similar to those of their corresponding G'. The loss modulus values were higher than the storage moduli for all 3 temperatures over the frequency range tested. This indicated the viscous characteristics were more dominant over the elastic characteristics. According to Morrison (2001), the crossover frequency can be used to determine a characteristic relaxation time of a polymer by taking the inverse of the crossover frequency. In the current work, the crossover frequency was invisible for PLA/PHB blends even at high frequency (100 rad/s). It seemed that the cross over could be achieved if the frequency higher than 100 rad/s was used. These behaviours were observed for all sample dynamic frequency tested. These results indicated that the PLA/PHB blends consist of the linear chain architecture, thus it took a very short time to relax after a deformation or stress was applied.

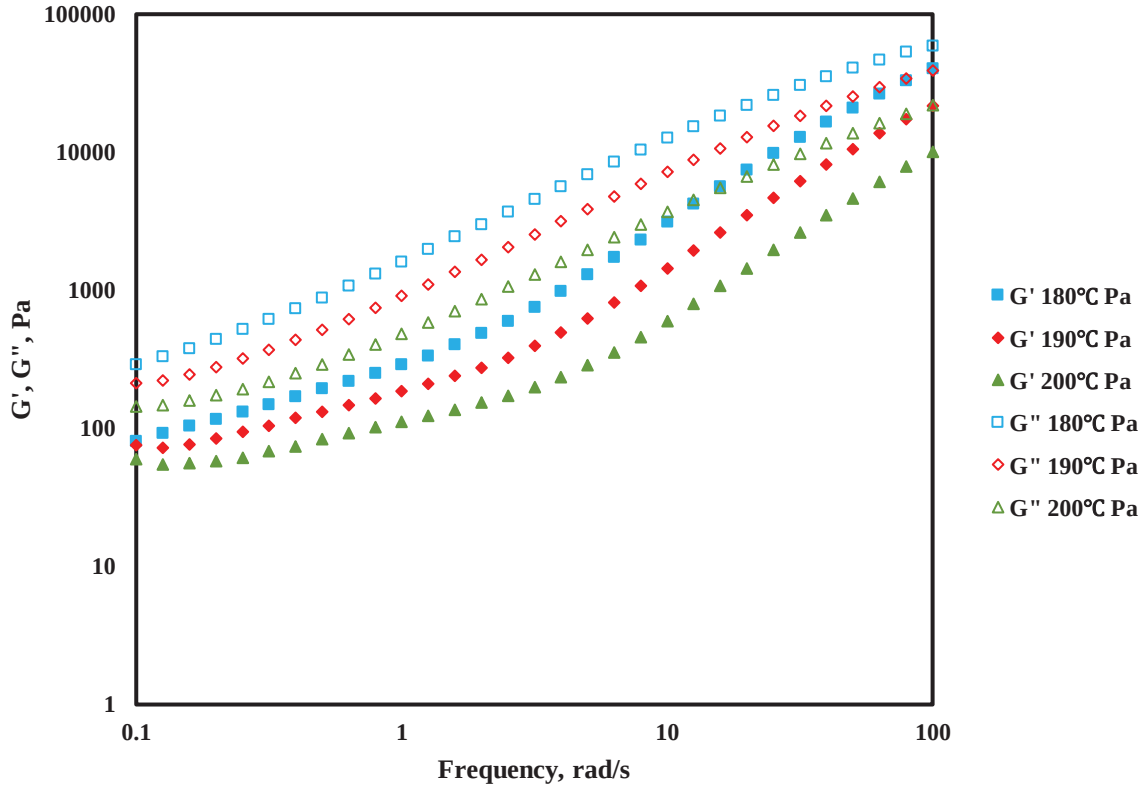


Figure 4. 5 Comparsion G' and G" of PLA80/PHB20 blends.

Figure 4.6 shows a comparison of η' of PLA30/PHB70 blend at three different temperatures (180, 190 and 200 °C). As expected, the viscosity decreased as the temperature was increased from 180 °C to 200 °C over the whole frequency range tested (0.1-100 rad/s). The blend at 200 °C exhibited more obvious shear thinning behaviour than that at other two temperatures. The thermal instability of PHB affected the viscosity of this blend (i.e. sharp drop at low frequency), especially at high temperature of 200 °C. After a plateau region, the blends at 180 °C and 190 °C showed a second shear-thinning behaviour which may be caused by disentanglement of the polymer chains. It led to an increased movement and subsequently lowered the dynamic viscosity. However, there is no obvious plateau region at 200 °C. It seemed that melt processing at a higher temperature affected PHB, leading to a degradation process.

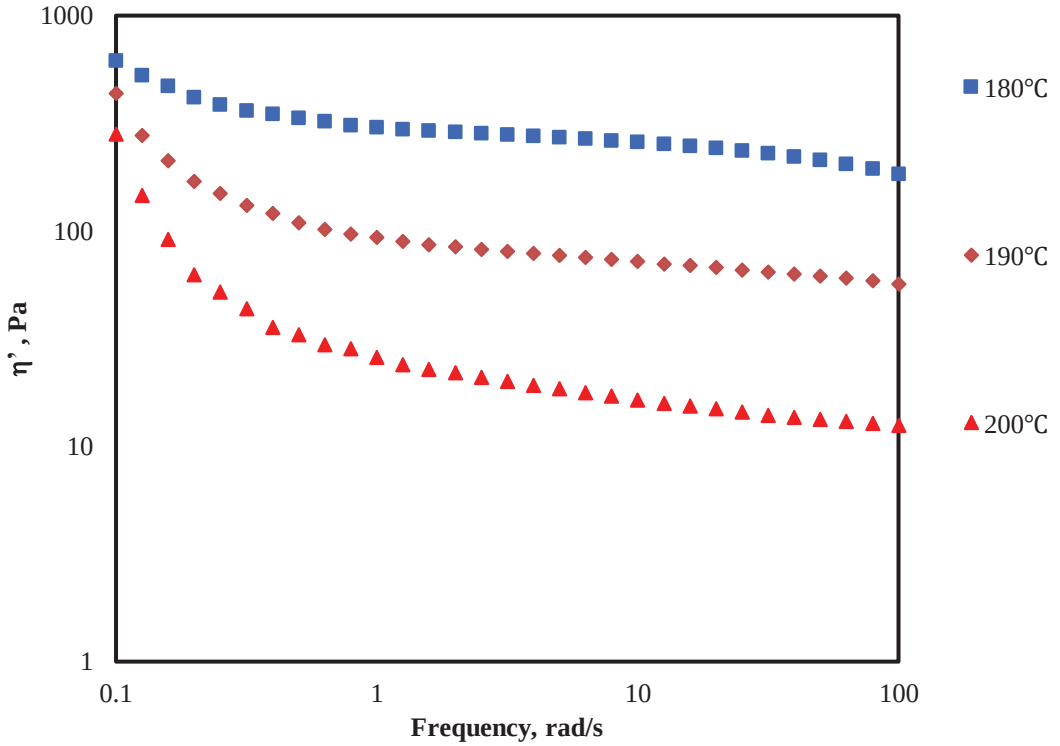


Figure 4. 6 Comparison of dynamic viscosity data of PLA30/PHB70 blend at different temperatures.

Figure 4.7 illustrates the storage moduli of PLA/PHB blends as a function of PHB concentration at three different temperatures and four different frequencies (0.1, 1, 10, and 100 rad/s). It is clear from Figure 4.7 (a) that storage moduli increased significantly as the PHB concentration was increased from 0 to approximately 20-25 wt%. The storage moduli of blends containing 25-50 wt% PHB then decreased significantly reaching a plateau where G' values were comparable to blends containing no PHB. The maximum G' value (peak) for each of the curve seemed to occur at the 20 to 25 wt% PHB. The actual values of G' at the peak for all curves were lower as the temperature was increased, as expected. It was also interesting to note that as the frequency was increased, the peak seemed to shift to the left (i.e. the peak occurred at a lower PHB content (at 20 wt% instead of 25 wt%). More stable and consistent trends were observed at 180 °C for all blends tested as compared to the higher temperature of 190 °C and 200 °C.

The storage moduli of PLA/PHB blends showed similar composition and temperature dependence with other rheological properties (G" and η'). As expected, blending PHB into PLA could increase the elasticity of the blends, which produced synergism in the storage modulus value of the PLA/PHB blends. The results showed integrated PLA/PHB blends, which provided significant evidence of optimum composition and temperature of blends for final packaging applications.

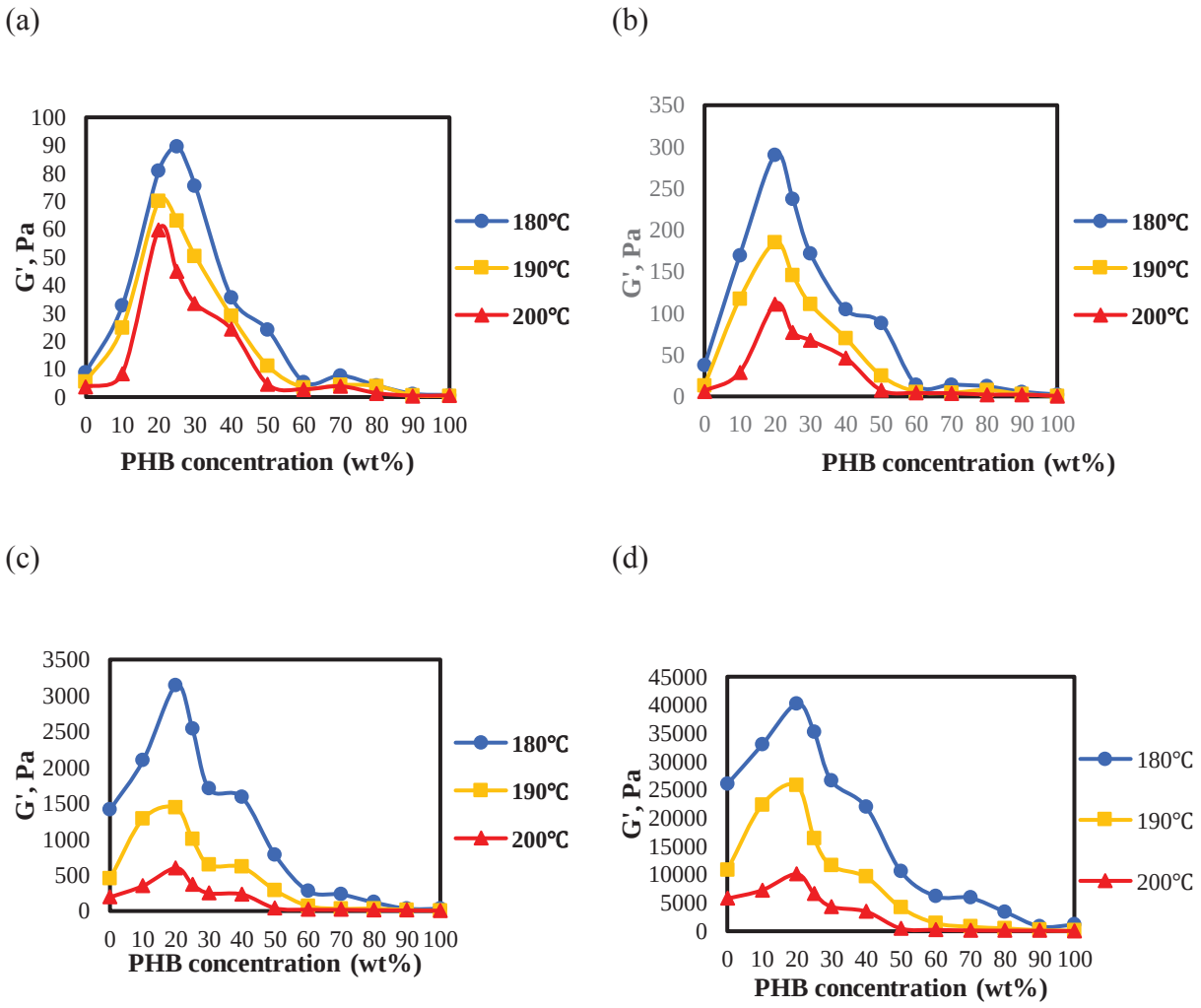


Figure 4. 7 Comparison of G' results at different temperatures and frequencies; (a) Frequency=0.1 rad/s; (b) Frequency=1 rad/s; (c) Frequency=10 rad/s; (d) Frequency=100 rad/s.

It was impossible to examine all required temperatures over a wider frequency range even the viscoelastic properties of PLA/PHB blends were temperature dependent. Therefore,

time-temperature superposition (TTS) principle was used to overcome this limitation. Under this TTS principle, data could be shifted to either a higher or lower frequency region than the actual frequency range tested. According to Sungsanit (2011), the TTS of viscoelasticity describes the dependence of viscosity on temperature as follows. It is pointed out that a change in the temperature from T_1 to T_2 does not affect the function dependence of η (viscosity) on γ and/or ω (frequency), but merely changes the zero-shear viscosity and the shear rate, occurred in the transition from Newtonian to pseudoplastic behaviour. With the increase of temperature, the viscosity curve at T_1, in the log (η) versus log(ω) plot, is shifted by a "shift factor" log(a_T) as show in Equation 4.1.

$$a_T = \frac{\eta_0(T_1)\cdot T_2 \cdot \rho_2}{\eta_0(T_2)\cdot T_1 \cdot \rho_1} \qquad (4.1)$$

Where ρ_1, ρ_2 denote the densities at temperatures T_1 and T_2, respectively. Accordingly, it is possible to construct a temperature master curve η(ω, T) from which viscosity curves for various temperature values may be obtained. The temperature effect on the viscosity function η(ω) is described in details by the Arrhenius law, (Dealy and Wissbrun, 1990). This law states that for thermo-rheological simple fluids the shift factor a_T is given by the Equation 4.2

$$\log a_T = \frac{E_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (4.2)$$

Where E_0 is the fluid activation energy in J/mol and R = 8,314 J/mol.K is the universal gas constant. It follows that if E_0 is known, the temperature master curve η(ω, T) can be constructed. In this investigation, TTS curves were constructed automatically from the experimental data by the ARES software.

The viscoelastic properties of the PLA80/PHB20 blends at 180, 190 and 200 °C are shown in Figure 4.8. Other blends at different concentrations behaved in a similar trend as well. The first shear-thinning behaviour of the dynamic viscosities (Figure 4.8c) occurred at low frequency range (< 1 rad/s). After a plateau region, the second shear-thinning behaviour occured after10 rad/s. The curves of G' and G" could eventually cross over at higher frequency (beyond 100 rad/s). So, it is necessary if the experiments could be examined at higher frequency.

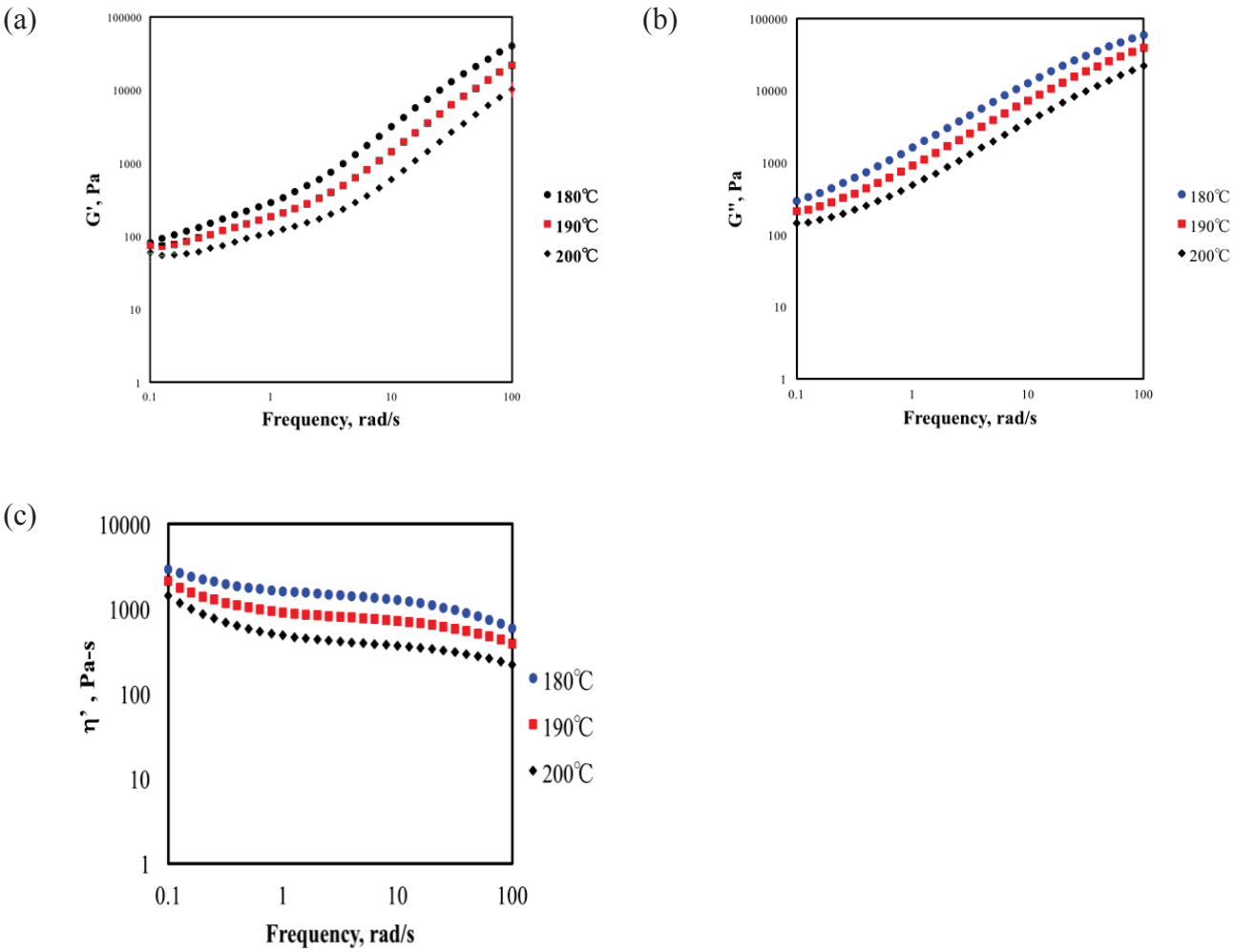


Figure 4. 8 Storage (a) and loss moduli (b), and dynamic viscosity (c) results of PLA80/PHB20 blend at different temperatures.

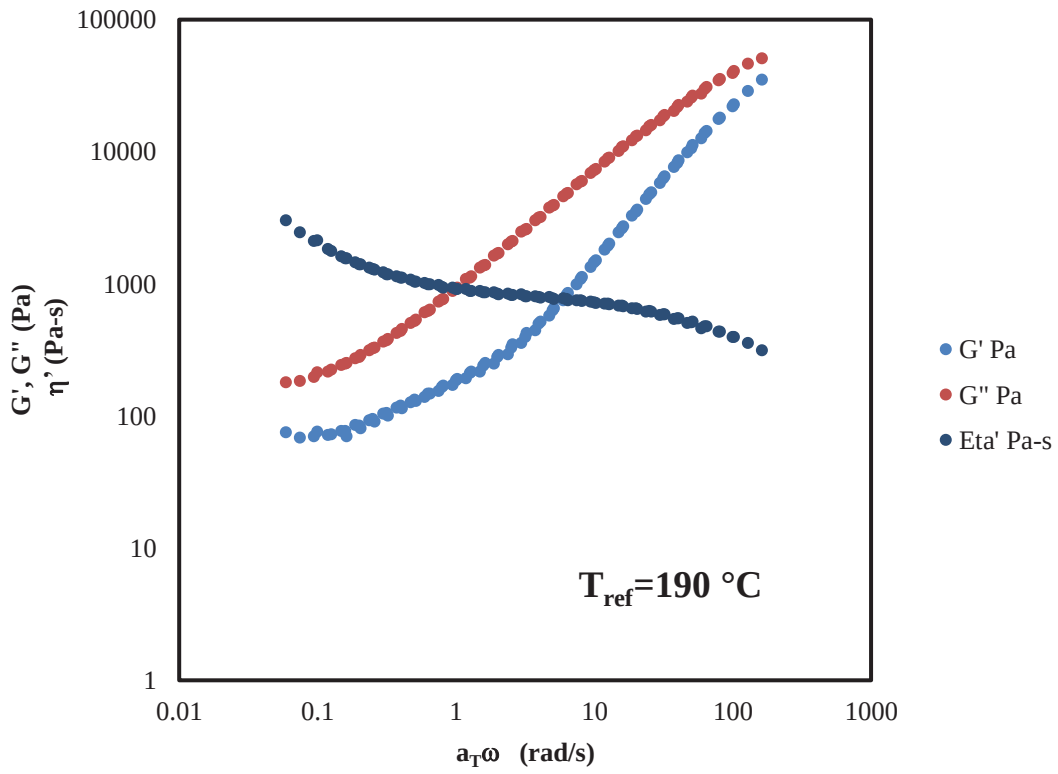


Figure 4. 9 Time-temperature superposition plot of PLA80/PHB20 blend. The master curve, with reference temperature of 190 °C, represents data at 180 °C, 190 °C and 200 °C.

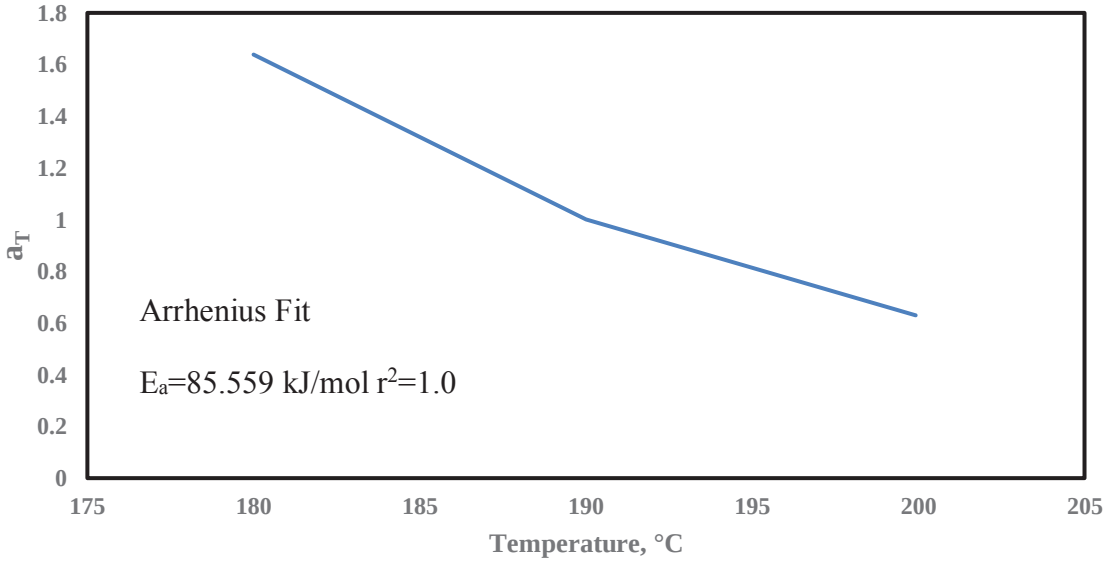


Figure 4. 10 TTS shift factors.

Figure 4.9 shows master curves created by time-temperature superposition performed on the PLA80/PHB20 sample. The master curve constructed used a reference temperature of 190℃ and was constructed from isothermal curves obtained at three different temperatures (180 ℃ , 190 ℃ and 200 ℃). It could be seen that, if compared to the original plots, the frequency range of the TTS plot was extended to both side - the lower and higher frequencies. This provided a clearer picture of the shear-thinning behaviour and the potential of G' and G" crossover frequency if higher frequency was used. The first and second shear-thinning behaviours still occurred at lower and higher frequency regions.

For non-Newtonian or shear thinning behavior, the power law model is the most common method used account for melt viscosity. Power law modle is shown in Equation 4.3.

$$\mu = K\dot{\gamma}^{n-1} \qquad (4.3)$$

Where K is the consistency and n is the power-law index. For the Newtonian behavior, n is equal to 1. In contrast, n varies between 0 and 1 for a shear thinning fluid (Gupta et al., 2006). The PLA/PHB blends obey a power-law modle with shear thinning behavior. The decrease in viscosity known as pseudoplastic behavior and also explains that the polymer chains are aligned and disentangled in the direction of the melt flow (Nitin, 2006).

4.3 Thermal Properties of PLA/PHB blends

Modulated differential scanning calorimetry (MDSC) thermograms of PLA/PHB blends are presented in Figure 4.11 and 4.12. The data for the glass transition (T_g), cold crystallization (T_{cc}), melting temperature (T_m) and the degree of crystallinity (X_c) of PLA/PHB blends are summarized in Table 4.1.

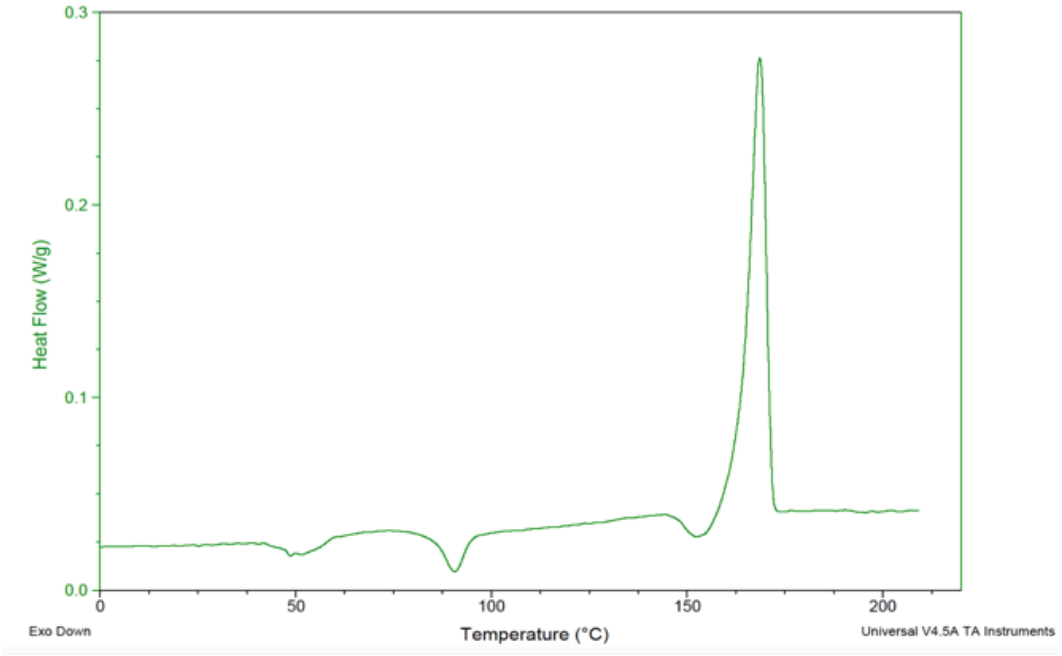
It has been found that pure PLA exhibited a glass transition around 60 °C, a broad cold-crystallization peak at 85-100 °C and a melting peak at 168.56 °C (Figure 4.11). The melting temperature of pure PLA was found to be 168.6 °C, which was similar to the value reported by Sungsanit (2011). Pure PHB exhibited an exothermal peak observed around 110 °C. The PLA75/PHB25 and PLA80/PHB20 blend showed a relatively strong recrystallization peak (Figure 4.12). The double melting peaks of Pure PHB could be due to the melting of "as-

formed" and recrystallized PHB crystallites (Hu et al., 2008). The double melting peaks also occurred in other PLA/PHB blends as well; the first one corresponded to the melting of the PLA component, and the other one corresponded to the melting of the PHB crystals formed. These results indicated that PLA/PHB blends were immiscible, which is consistent with the results of previous studies (Hu et al., 2008 & Zhang et al., 2010). Moreover, the recrystallization peaks could be seen in all PLA/PHB blends, which indicated that the addition of PHB could recrystallize PLA in all blends. The blends with low PHB content showed a strong recrystallization peak, which was due to small finely dispersed PHB crystals acting as nucleating agents in PLA (Furukawa et al., 2005 & Zhang et al., 1995).

It is worth noting that Zhang (2010) reported there were three peaks of melting temperature in the melting process: the lowest temperature peak, which corresponded to the melting of PLA; the next peak corresponded to the melting of the "as-formed" PHB crystallites during the process; and the highest peak corresponded to the melting of the PHB crystals form from the recrystallization. However, in this study, the MDSC thermograms showed two melting peaks in the second heating cycle. It could be due to the low melting peak overlapping with the melting peak of PLA as they laid in the same region. The occurrence of the two melting peaks has been reported and confirmed by Furukawa et al., (2005) and Hu et al., (2008). They reported that the multiple melting peaks resulted due to melting, re-crystallization and re-melting process. The high melting peak occurred due to rearrangement of crystal morphology and the low temperature melting peak was due to the melting of original crystals when PHB was cooled from the melt.

During the cooling process, the crystallization peak of PLA could not be clearly observed, whereas pure PHB showed a crystallization peak. These results indicated that the crystallinity and crystallization rate of PHB was much higher than that of PLA. Moreover, crystallization peak of PHB could not be observed in the blends containing low content of PHB, but could be seen in the blends containing high content of PHB (>50 wt%). This indicated that PHB did not crystallize much in the low content of PHB during the cooling process.

(a)



(b)

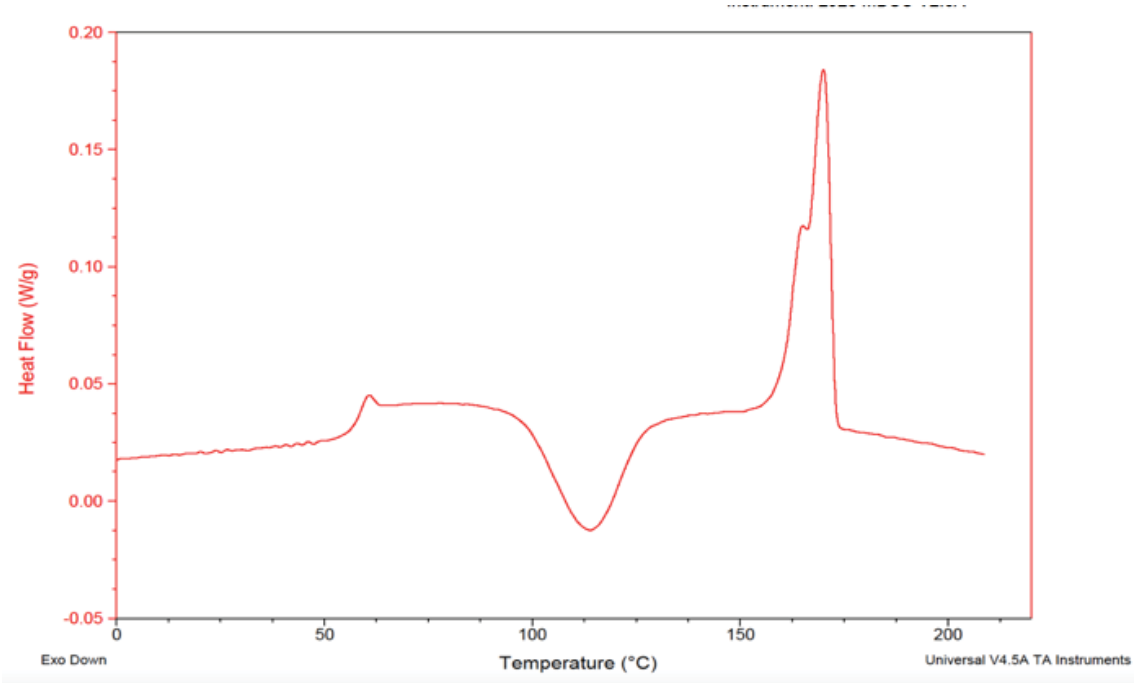
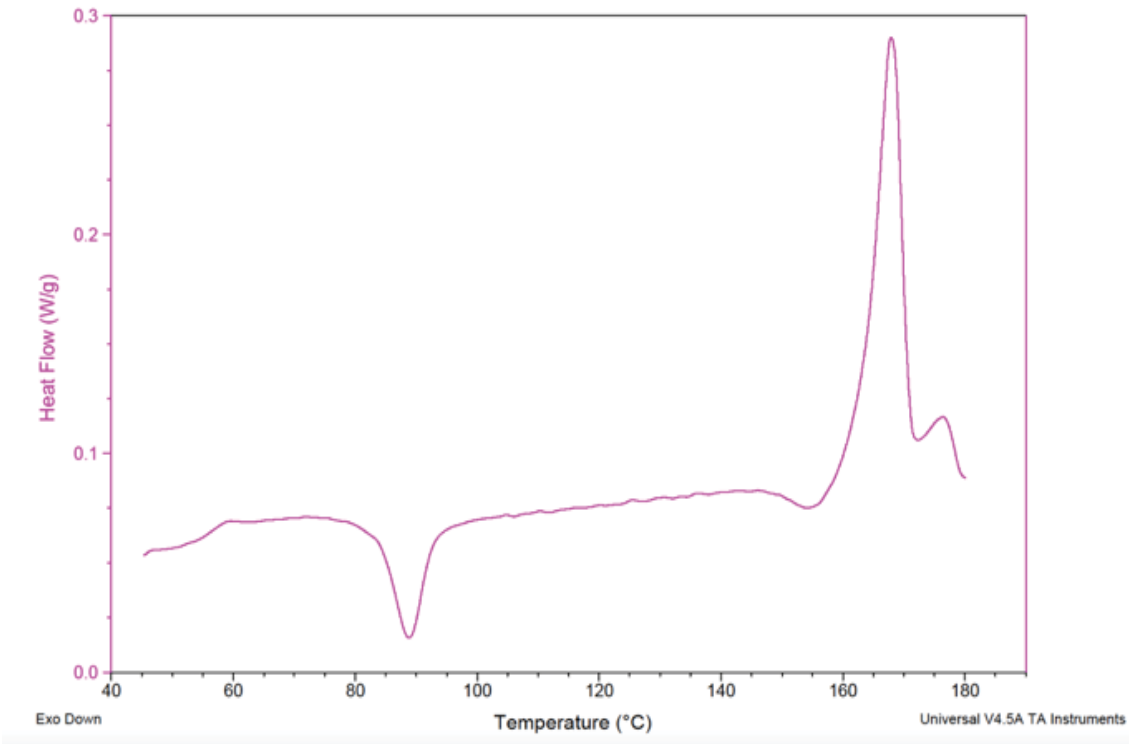


Figure 4. 11 MDSC results of PLA/PHB blends: (a) PLA100/PHB0 (b) PLA0/PHB100 obtained from the second heating cycle.

(a)



(b)

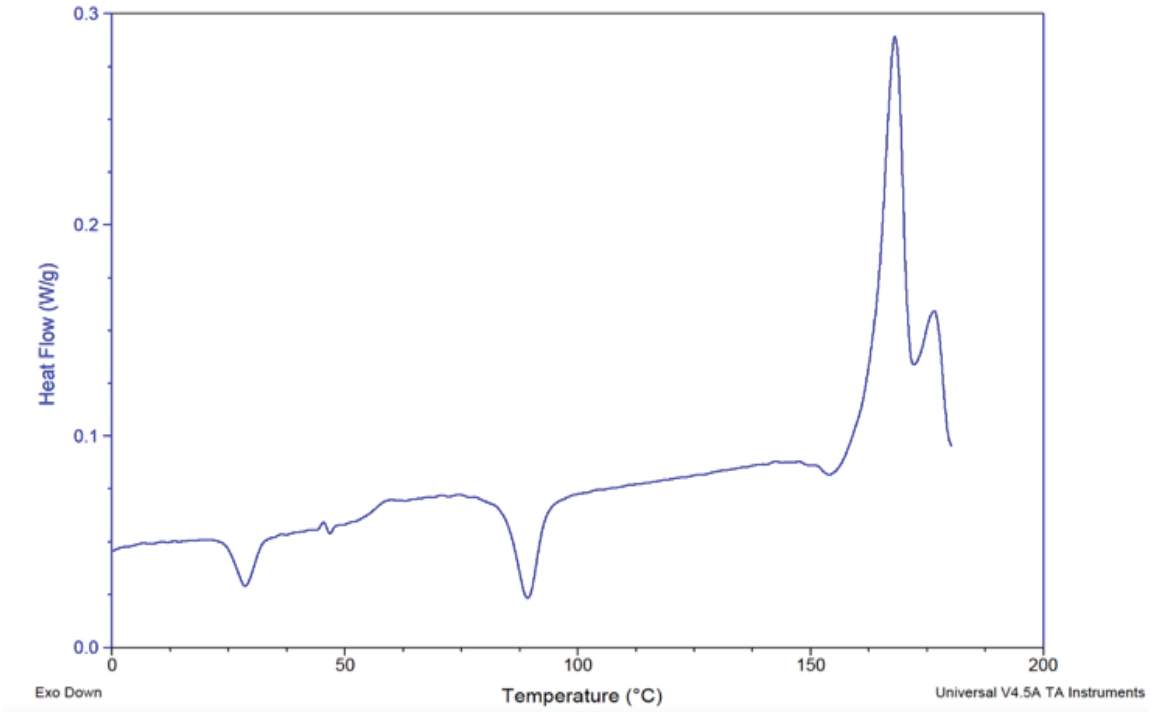


Figure 4. 12 MDSC results of PLA/PHB blends: (a) PLA80/PHB20 (b) PLA75/PHB25 obtained from the second heating cycle.

A summary of the T_g values as well as other thermal parameters are given in Table 4.1. According to Reinsch et al. (1997), the enhancement of the nucleation rate reduces the

temperature of cold crystallization and thus reducing the overall rate of cold crystallization. It was observed that T_{cc} values decreased as the PHB content in the PLA/PHB blends increased, because the addition of PHB shifted T_{cc} peaks to lower temperature as compared to the T_{cc} peak of pure PLA. A reduction in T_{cc} suggested that the addition of PHB supported recrystallization of PLA (Hu et al., 2008). An increase in PHB concentration enhanced the nucleation rate and hence reduced cold crystallization (Furukawa et al., 2005). The percent crystallinity is determined using the following Equation 4.4.

$$\% \text{ Crystallinity} = \frac{(\Delta Hm - \Delta Hc)}{\Delta Hm^{\circ}} \times 100\% \qquad (4.4)$$

Where ΔH_m is the heats of melting and ΔH_c is the cold crystallization in J/g. The ΔH_m° is a reference value and represents the heat of melting if the polymer were 100% crystalline. In this study, the change of enthalpy of pure PLA is 93 J/g and 146 J/g for pure PHB.

The X_c increased with increasing PHB content from 0 to 75 wt% (51.4%), but decreased as PHB content was increased. This could be due to PHB acting as a nucleating agent in PLA (Zhang et al., 2010). The increased X_c values with the addition of PHB could be related to the fact that the high crystalline structure of PHB presented in PLA/PHB blends restricted the free mobility of the semi-crystalline PLA polymer chains. This induced the nucleation and crystallization of the PLA component in the PLA/PHB hence increasing the X_c value (Zhang et al., 1995).

Table 4. 1 MDSC thermal properties of PLA, PHB and PLA/PHB blends

Sample	T_g (°C)	T_m (°C)		T_{cc} (°C)	$\Delta H_m°$ (J/g)	X_c (%) PLA [a]
		T_{m1} (°C)	T_{m2} (°C)			
PLA100/PHB0	58.3	168.6	-	88.7	93	35
PLA80/PHB20	55.9	167.8	177.2	87.6	103.6	38.9
PLA75/PHB25	53.1	168.1	176.7	83.5	106.25	40
PLA25/PHB75	45.9	167.4	171.4	68.6	132.75	49.9
PLA0/PHB100	-	-	170.1	112.5	146	63.2

[a] X_c (%), calculated using $\Delta H_m°$ of PHB of 146 (J/g) and $\Delta H_m°$ of PLA of 93 (J/g)

It can be concluded that the PLA/PHB blends are immiscible, and the crystallization of PLA in the blends increased with the addition of PHB, up to 25 wt%.

Chapter 5 Conclusion and Recommendations

Inherent brittleness and low toughness of PLA has been problematic in terms of processing and also have limited PLA's use in certain industries. This main focus of this Master's thesis was to study the rheological and thermal properties of PLA when blended with another bio-based polymer such as PHB.

It has been confirmed by MDSC that the investigated PLA/PHB blends were immiscible, but there existed molecular interaction between two polymers over the entire composition range. The blends exhibited two remarkable separate melting temperatures, corresponding to the melting temperature of pure PLA and PHB. The crystallization of PLA in the blends increased with the addition of PHB, up to 25 wt% (optimum value); then decreased significantly to 60 wt% PHB; and finally approaching constant values from 60-100 wt% PHB content. This was due to the relatively high crystalline structure of PHB, which acted as a nucleating agent in the PLA matrix. The recrystallization temperature reduction suggested that the addition of PHB supported recrystallization of PLA.

Rheological results indicated that the blends showed positive-deviation (synergistic behaviour), according to the mixing rule, at low PHB content (0-40wt%). They possessed liquid-like, temperature-dependency and shear-thinning behaviour. The optimum rheological properties (storage and loss moduli and dynamic viscosity) of the PLA/PHB blends were obtained for blend containing 20-25 wt% PHB.

Therefore, based on the rheological and thermal results, the optimum concentration of blend and temperature to be used in producing material for packaging application, would be PLA80/PHB20 and at 180 °C, respectively.

The following recommendations for future work are highlighted:

- Conduct morphological and mechanical properties of PLA/PHB blends for final application.
- Examine other grades of PLA to compare the effect of the different grades on rheological and thermal characteristics and properties.

- Use the PLA80/PHB20 blend to produce packaging film and determine its properties.
- Investigate the addition of another material to the PLA/PHB blend, such as nano-crystalline cellulose (NCC), microfibrillated cellulose (MFC) or micro-crystalline cellulose (MCC).
- Investigate the degradation behaviour of the PLA/PHB films in various environments.

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APENDIX A

Dynamic frequency results of PLA/PHB blends at 190 °C.

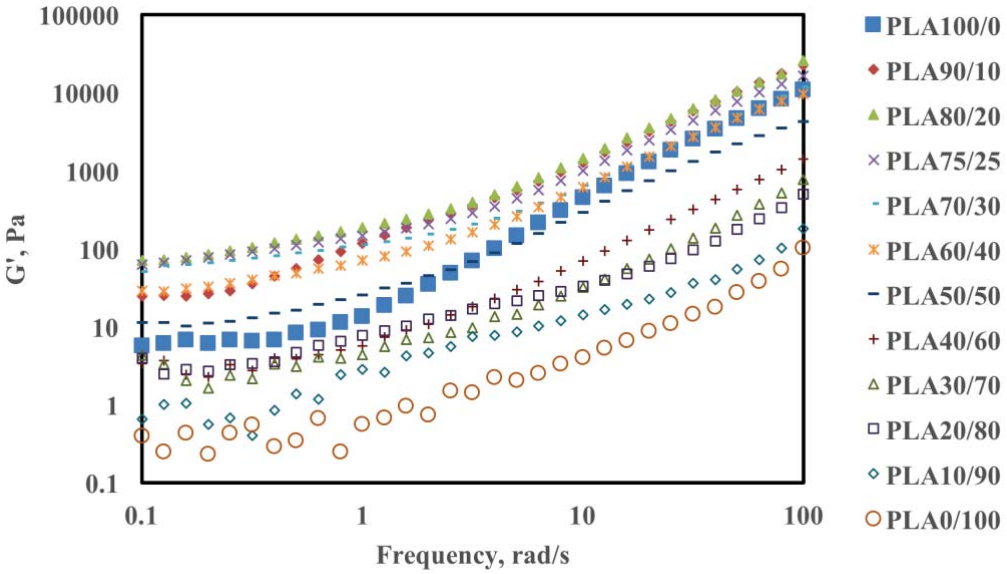

Figure A. 1 Comparison Storage modulus (G') of PLA/PHB blends at different concentration at 190 °C.

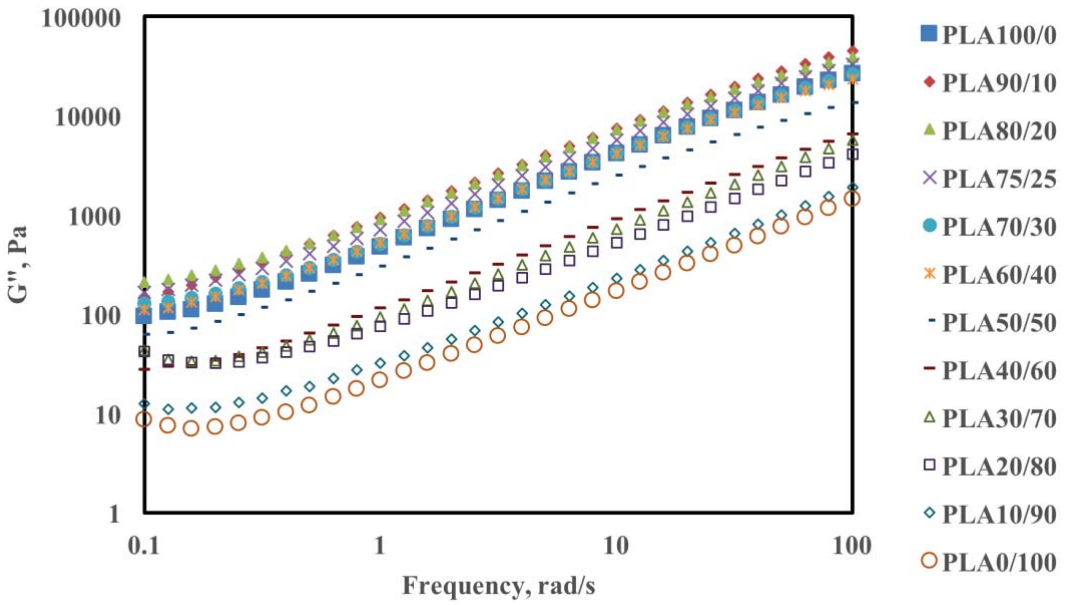

Figure A. 2 Comparison Loss modulus (G") of PLA/PHB blends at different concentration at 190 °C.

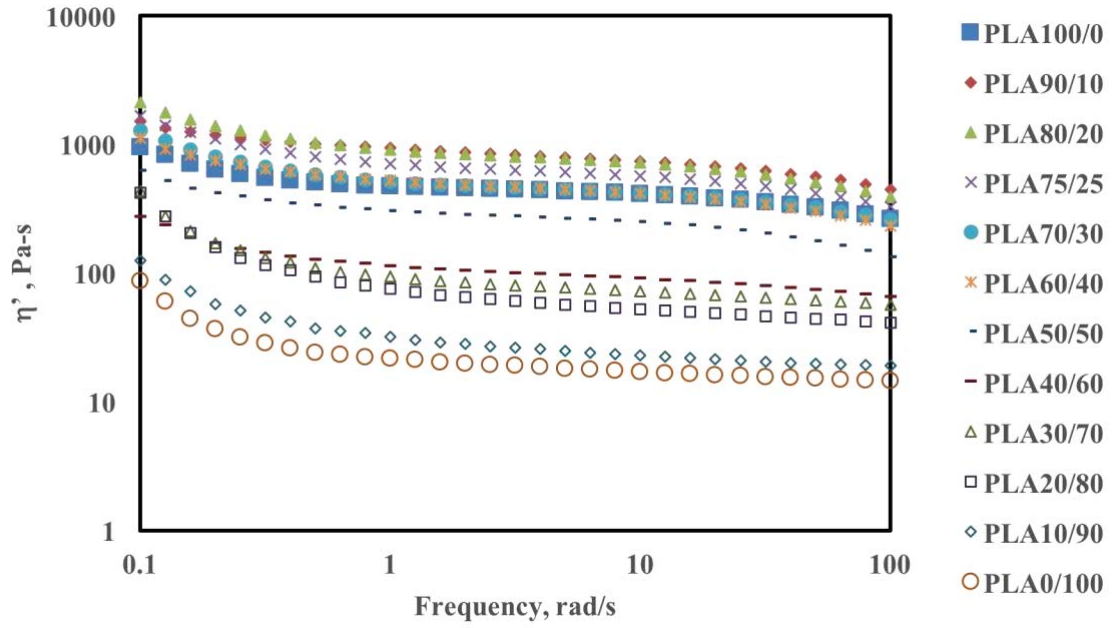

Figure A. 3 Comparison of Dynamic viscosity (η') of PLA/PHB blends at different concentrations at 190 °C.

Dynamic frequency results of PLA/PHB blends at 200 °C.

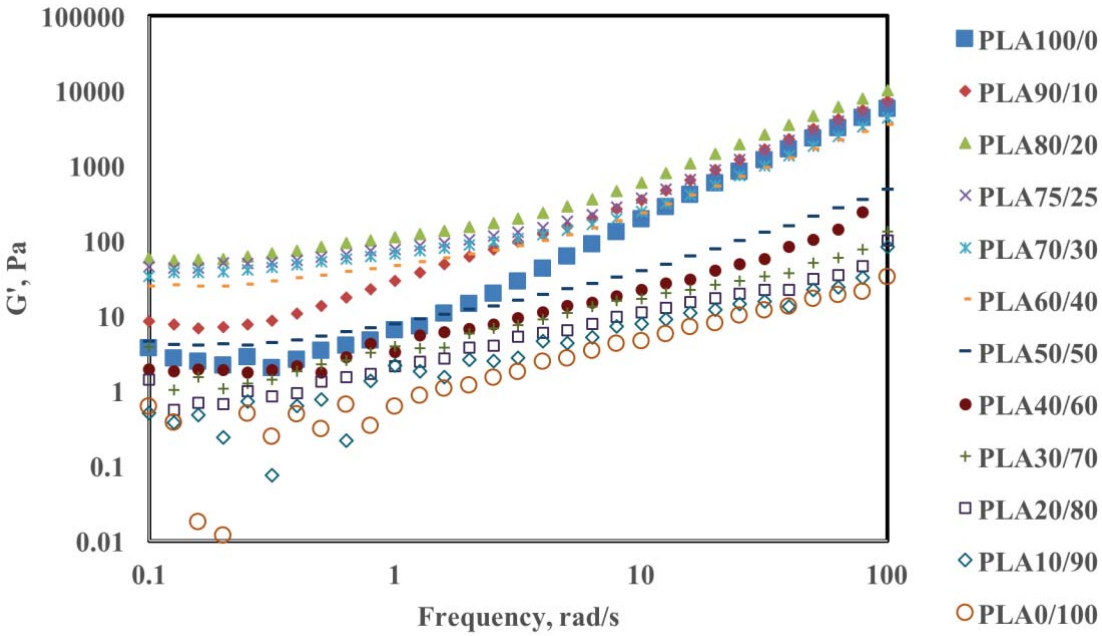

Figure A. 4 Comparison Storage modulus (G') of PLA/PHB blends at different concentration at 200 °C.

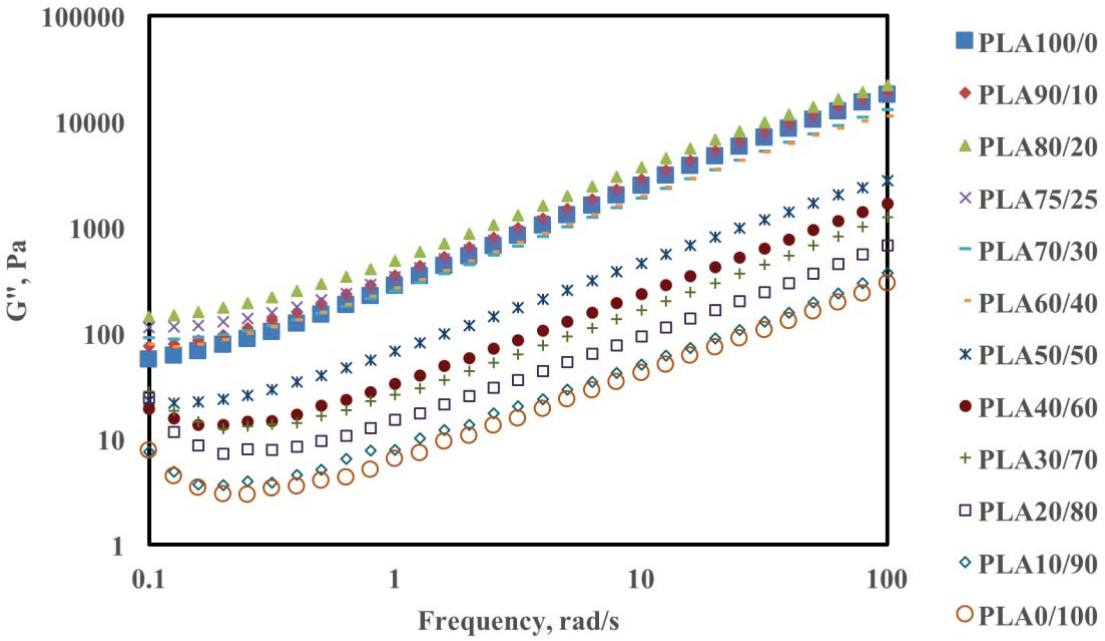

Figure A. 5 Comparison Loss modulus (G") of PLA/PHB blends at different concentration at 200 °C.

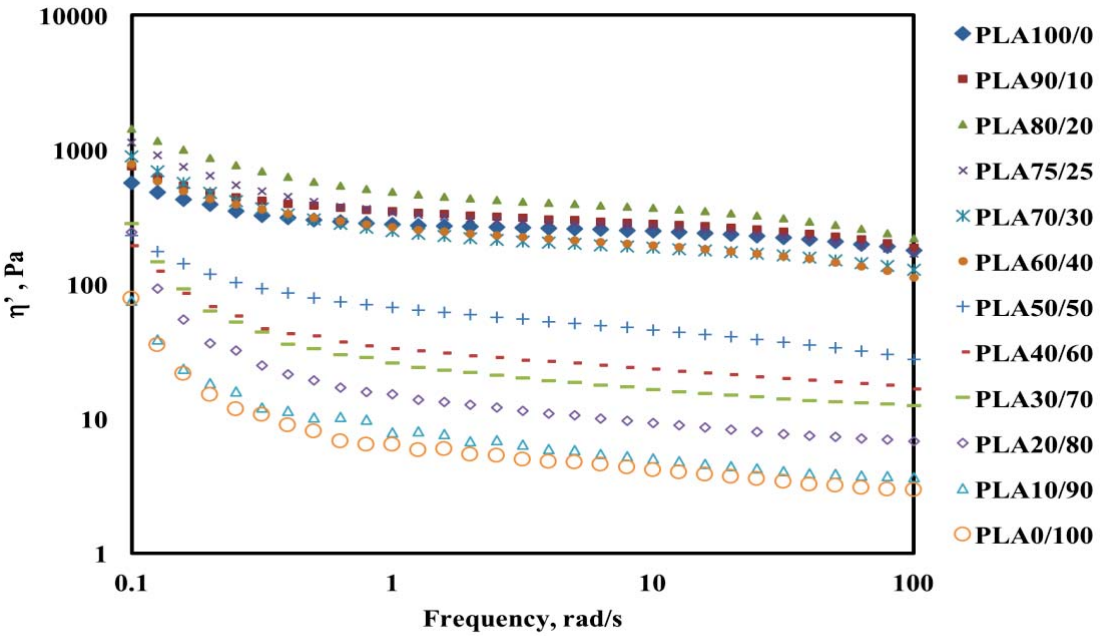

Figure A. 6 Comparison of Dynamic viscosity (η') of PLA/PHB blends at different concentrations at 200 °C.

APENDIX B

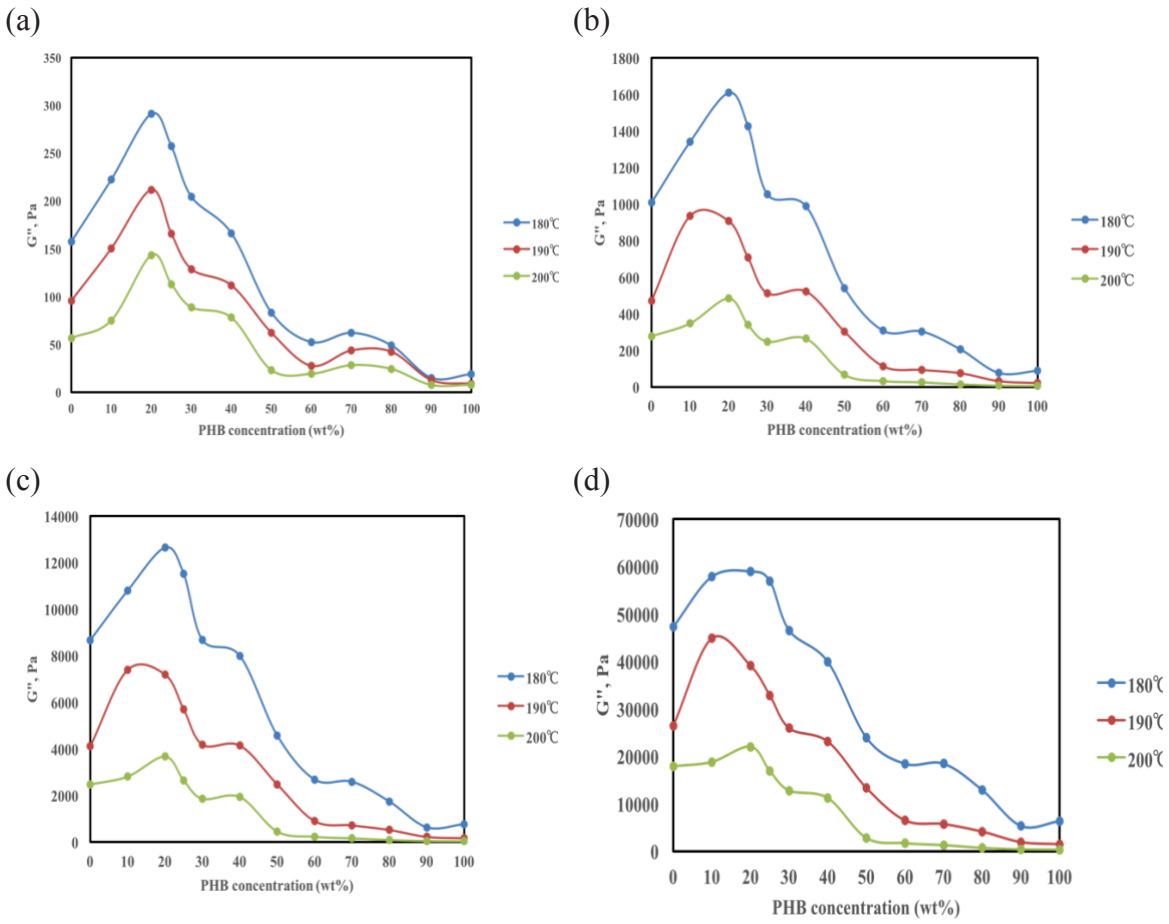

Figure B. 1 Combination of PLA/PHB G" comparison (a) Frequency=0.1 rad/s (b) Frequency=1 rad/s (c) Frequency=10 rad/s (d) Frequency=100 rad/s

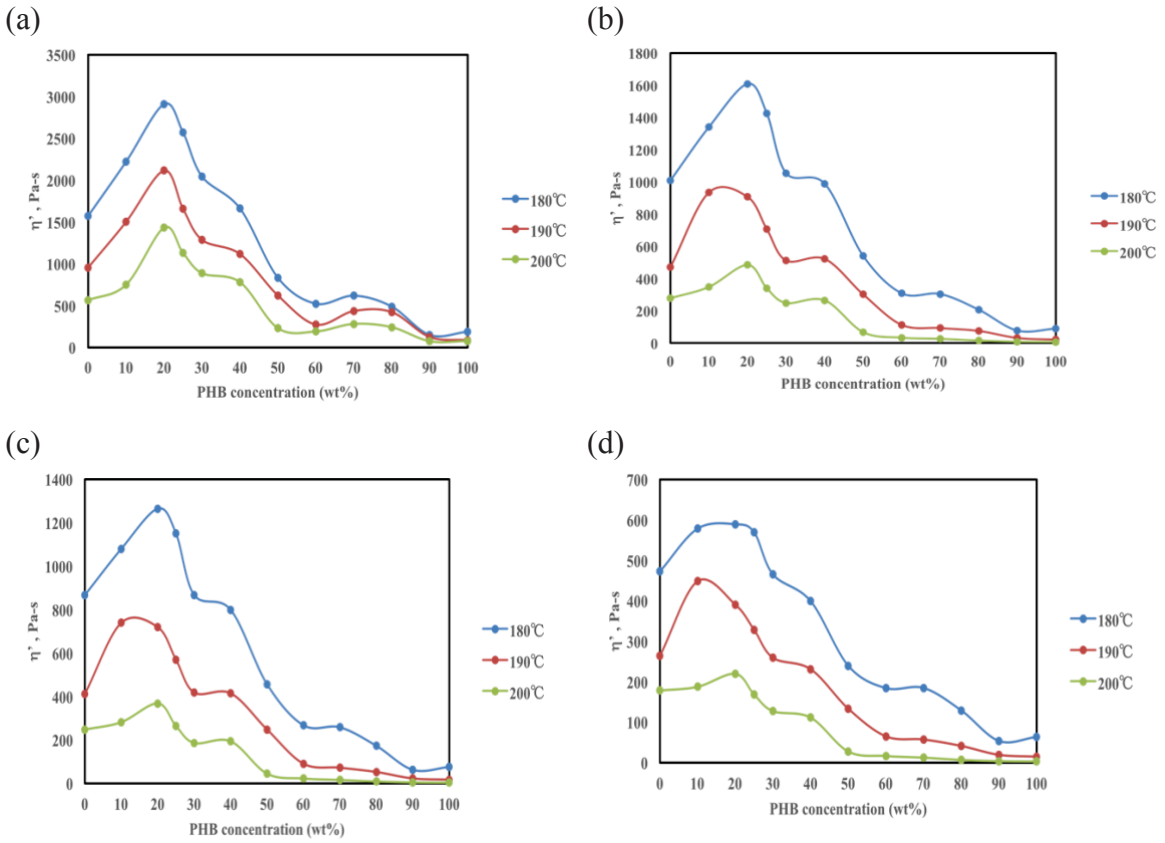

Figure B. 2 Combination of PLA/PHB η' comparison (a) Frequency=0.1 rad/s (b) Frequency=1 rad/s (c) Frequency=10 rad/s (d) Frequency=100 rad/s